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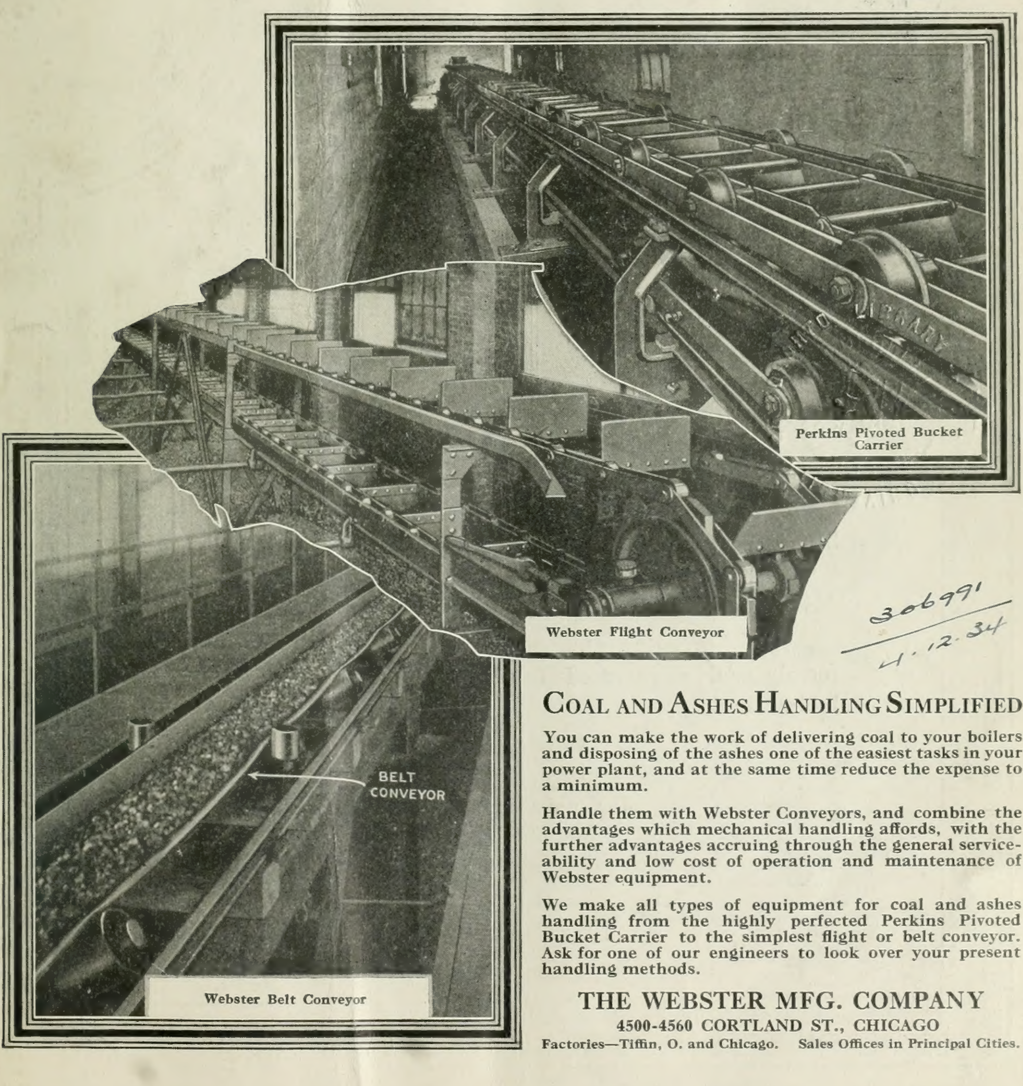

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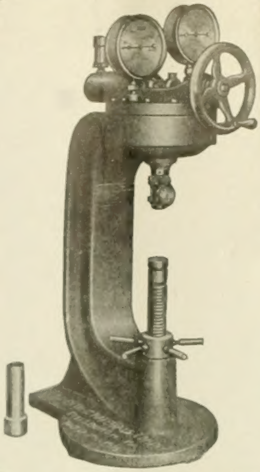

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EDITORIALS

Now—All Together!

SO MUCH has been accomplished in the passage by the Senate of the paragraphs in the tariff bill relating to coal-tar intermediates and dyes that we must make a final effort *now* for the embargo. We are rapidly passing out of the period when people generally were clamoring for American industries and were willing to go to what they considered great lengths out of patriotic motives. To-day the principal object seems to be to buy as cheaply—anywhere—as possible and to sell at the top price.

But actual conditions have changed little. Imported materials are offered on a low price basis more often than upon high quality. In his first newspaper interview a recently arrived ambassador took occasion to condemn our dyes and praise those of his country.

That the Senate saw fit to pass the paragraphs mentioned indicates a great gain notwithstanding many difficulties. The way the duty on scientific apparatus was reduced from 55 per cent to 35 per cent in about two minutes with some ten senators on the floor indicates the many slips possible. If you have not expressed your views to your senators and representatives, do so now. If you have urged favorable consideration of the whole chemical program, send in a reminder.

Much has been gained. The day can be won if we all work together, and now!

Textile Research Institute

IN THE hearings before the Senate committee investigating dyes, the statement was made that there remain to be invested in education and research several hundred thousand dollars representing the profits of the Textile Alliance, in accordance with the original understanding with the State Department.

We urge that this fund be devoted to the establishment of an American Textile Research Institute. Notwithstanding the work of government bureaus, private corporations, and textile schools, there are concerted efforts abroad which surpass anything we have to offer. As an industry, textile manufacturers have not yet been convinced that they can conduct research as an association enterprise. We believe that unless the present opportunity is utilized it may be many years before adequate work will be supported here.

A simple effective plan can be devised. Cotton, wool, linen, and silk should be represented in the institute. There are strong trade associations representing these fibers. There is a splendid association of finishers, and still other groups of spinners, dyers, dry cleaners, laundrymen, and other crafts directly concerned with textiles. From these groups a strong advisory committee can be formed and by utilizing the income from the fund to be available a deal of important work can be carried on in existing laboratories throughout the country. The initial staff of the institute could consist of a director with proper assistants, and if desirable an early activity could be the establishment of informational service and a statistical bureau and a proper medium for broadcasting new information.

To divide the capital sum among those now interested in textile research seems to us unwise, for provision should be made for study of new problems as they may arise in whatever laboratory may be best fitted for the investigation. By keeping the present sum as a fund other money is sure to be attracted, and there would be available annually a sum which under wise administration would eventually bring to the laboratories far greater support.

Plans should be perfected, and it is our hope that the committee appointed by the Textile Alliance to consider and recommend methods for the employment of the money in hand may decide upon some such program as we have here suggested.

The Chemical Exposition

NO ONE can doubt that the chemical exposition has played a useful part in promoting chemical industry in our country. We are approaching the Eighth National Exposition of Chemical Industries. Let us consider whether changes in plan could be made to advantage.

The exposition serves as a medium for the exchange of ideas between exhibitors and the purchasers of their products. It has an important educational function to perform, and it assists in creating the proper conception of the chemical industry in the minds of the public.

While the tendency has been to perform these services, we believe much remains to be accomplished. Many of the exhibitors are just beginning to see the possibilities of such an exhibition. Others fail to find in the present plan enough to gain their further support. We suggest therefore that the time has come when the four groups representing the industry should be brought into closer coöperation with the exhibition management and that the undertaking should be made a coöperative project. The Manufacturing Chemists' Association, the Synthetic Organic Chemical Manufacturers Association of the United States, the Association of Scientific Apparatus Makers, and the recently formed Chemical Equipment Association include the majority of those who are directly and financially interested. With this group could be associated as advisers representatives of scientific societies and others in a position to contribute to the success of the exhibit.

We should like to see an effort made to conduct an impersonal educational type of exhibit where the public could be interested in the science as a whole rather than in individual products. Many methods of treatment suggest themselves in this day of expert model makers, motion pictures, and other devices. Either concurrently with this exhibit or separately, there could be held a technical exhibit for that portion of the public, both buyer and seller, who can appreciate the strictly technological phases of the industry. The first would be for the purpose of education, the second for the purpose of improving devices and obtaining orders.

Much can be done to improve the coming exposition if the exhibitors will take pains to place in their booths materials which will really contribute to the interest of the show as a whole and do something toward educating the public.

It is false economy to invest comparatively large sums in space and then fail to show products or demonstrate processes, and especially to place in charge those who are not sufficiently well informed to represent the exhibitor. In the past some exhibits have been in charge of men incompetent to answer questions and make explanations. It is very much like buying expensive advertising space and then designating the office boy to write the copy. First impressions, whether obtained through the character of the exhibit or through the representative in charge, are likely to be lasting, and for several exhibitors the exposition is their only contact with a considerable part of the public.

Facts in Plain Words

CHEMISTS who read beyond their own field have perhaps seen the paper of George Otis Smith, Director of the U. S. Geological Survey, in *Economic Geology* for January-February 1922. Under the caption "Science, the Oracle," Dr. Smith urges geologists to set forth facts in the simplest possible form, being convinced "that at its best, science is simple—that the simplest arrangement of facts that sets forth the truth best deserves the term scientific." Dr. Smith uses several examples from geological literature to show how frequently words are used for their own sake, and the failure of authors to realize the need of reaching their readers through words more easily understood than the technical phrases so dear to many of us. Thus, " 'disseminated' and 'disintegration' are words that please every ear, trained or untrained, while the garden variety of mind is helped along by the plain words 'scattered' and 'breaking up.' "

In chemistry it should be possible for us to state our facts in words sufficiently plain to make them easily understood without introducing that extreme form of popularity which is distasteful to many scientific writers. How often we fail to interest the layman in a subject which really concerns him, merely because we persist in concealing our thoughts behind a barrage of professional phrases. Most of us are pleased when we find a dentist, a physician, a lawyer, or a banker who will discuss his work with us in terms which we understand. If we desire to have our science understood and appreciated, ought we not to be willing to do as much for them?

SEVERAL of our presidents have had the opportunity to visit a number of Sections of the Society, but so far as we know none has traveled more widely in the interests of the Society than has President Smith. We have followed him in some places and had the good fortune to be with him in others. It is certain that his visits have done a great deal to promote the interests of the Society and to assist chemists in each locality. His delightful discussions of various phases of historical chemistry in America have given the younger men ideals toward which to look and traditions of earnest constructive work to uphold. He has urged colleges to write the history of their chemical departments now, with additions to be made from time to time in future, so that some future historian may have better facilities in painting a true picture of chemistry in America. His talks with teachers as well as with students have been inspiring. President Smith has done much in his travels for chemists and the American Chemical Society.

Scientific Research an Association Activity

IT WAS recently our pleasant task to review before the Institute of Margarin Manufacturers the tendency in America to-day for trade associations to undertake scientific research as one of their productive activities. Among the hundreds of trade associations in this country, many of which engage upon work of standardization, there are some thirty-five which have become identified with particular scientific problems. These associations vary between such extremes as four and 12,500 members. The budgets are supplied by assessment or contributions and are from $2500 to several hundred thousand dollars. While we have always maintained that an industry derives the greatest benefit from research when it is made a definite and adequately supported part of its own organization, it is coming to be accepted that many fundamental problems can be most thoroughly studied on a basis which calls for coöperation among firms rather than excessive expenditure by a single corporation.

It is encouraging to find several important associations originally organized for nonscientific activities turning to constructive plans for research and technical training. The experience of the associations that have been engaged in research for a number of years has encouraged others to venture upon programs of their own.

The Institute of Margarin Manufacturers is developing plans for early attention.

The Institute of American Meat Packers is now considering an ambitious plan whereby it may become so organized as to combine a research institute, an educational institution, and an industrial museum with a trade association. Those who heard the address of Mr. Thomas E. Wilson before the General Meeting of our Society at Chicago will not be surprised to find him chairman of the Plan Commission of the Institute.

It generally follows that those who derive the greatest benefit from association research are those with the best trained technical staff. To our mind, the ideal is the continuance of fundamental research as a group project with the utilization of its products by the individuals of the group, each according to his own needs and through his own scientific organization.

Dating Scientific Books

AT THE Birmingham Meeting the Council passed a resolution calling upon publishers to print the dates at which chemical books are written or revised rather than the date copyrighted or the date printed, so that the purchaser may have some guide in selecting recent contributions to the literature. This resolution has been sympathetically received on the whole by the publishers in our field.

Many publishers have expected readers to ascertain whether a book has been revised by consulting the copyright date or the date of the last preface. Others designate a book as the first edition with a title page date beneath the imprint and continue to designate this work as the first edition without change of title page date, using for example, first edition, second impression, or third impression as the case may be, until the book is thoroughly revised. At such time the title page date is of course changed. This is obviously what we desire, and publishers should refrain from changing the title page date whenever the book is merely reprinted.

Publishers, like other tradesmen, comply with any insistent reasonable demand. Book buyers can have books properly dated if they want them.

Engineering and Conservation

THE PART played by research in conservation has been the subject of many an article in which the importance of new studies has been emphasized. The application of acquired knowledge in the effort to conserve natural resources ought to be an established practice in engineering, but of late the desire to reduce first costs appears to have led many automotive engineers away from this sound principle. It is disturbing to find strong light-weight materials being displaced by heavier ones in the interests of low first cost without regard to what is involved in transporting the greater weight during the life of the car. In a certain well-known car a few dollars have been saved in construction at an expense of power efficiency estimated by different specialists at from 20 to 50 per cent. When the number of these cars is multiplied by the amount of fuel which could be conserved annually by a slightly higher first expenditure, we are led to suggest legislation, if necessary, to compel all manufacturers of automotive vehicles to include in their designs such principles as experience has taught will contribute to direct saving of petroleum products.

The indifference of automotive engineers to the problem of future fuels is well known. Cars are continually built as if gasoline as it used to be would last forever. That may be justified because a gasoline substitute has not been produced on a commercial scale, although motorists know the changing characteristics of what they buy as gasoline.

Realizing the importance of the liquid fuel situation, the Société de Chimie Industrielle of France has called an International Congress on Liquid Fuels, to be held in Paris. Further information is given on page 631.

So far as obtaining the maximum power from present fuels is concerned, the question of saving a few dollars in construction should certainly be made subordinate, particularly by those manufacturers who claim to have exalted ideals where public welfare is concerned.

OUT IN Tacoma the Olympic Chemical Club has created an executive body of six members to coöperate with other civic organizations in the upbuilding of the community. This chemical engineering council for public welfare acts independently of the Olympic Chemical Club, but its members are individually responsible to the Club. The council will aid in the establishment of desirable new industries, assist established industries in developing along sound and proper lines, and be active in all matters relating to health and safety in which the science of chemistry plays a part. The education of the public to a better appreciation of chemistry, the ethics of chemists and chemical engineers, the protection of the public from being victimized by promoters in matters pertaining to chemistry, the study of local industrial resources in order that data may be supplied to those interested in establishing industries are other objects. Other Sections and chemical clubs may find it well worth while to consider this example which they may wish to follow.

ALTHOUGH we travel as much as our budget will allow, we can serve the science and the industry to much better advantage if we can be kept informed regarding the opinions, desires and accomplishments of individuals and Local Sections in the SOCIETY. In an effort to achieve our ideal the Local Sections have been asked to appoint official staff correspondents for THIS JOURNAL. Our list is not yet complete, but the names of the correspondents who have been appointed are given on page 653.

Texts

HAVE YOU read the preface written by Dr. E. E. Slosson for the revised edition of Smith's "Intermediate Chemistry?" In a few pages this interesting writer has given us texts sufficient for a whole series of lectures scientifically sound and popular in their appeal. Or those who share the view expressed by W. L. L. in the *Chemical Bulletin* for June will find in these thoughts suggestions for really scholarly addresses in which to teach *about* chemistry rather than to teach all men chemistry.

> "Chemistry is the science of power. All the energy of man and beast and all the energy of machinery, except that furnished by windmills and water wheels, is chemical energy and nearly all of this is derived from two simple and similar chemical reactions, the oxidation of hydrogen to form water and of carbon to form carbon dioxide."
>
> "Chemistry has control of life and death. An animal or plant deprived for a time of the proper chemical compounds will starve or if it imbibes a minute amount of the wrong chemical compounds it dies at once."
>
> "Chemistry is the science of terror and pity" for it provides both the materials for destruction and for healing. It is man's weapon against disease, insects, fungi, pain, and sleeplessness. It tears down and builds up.
>
> "Chemistry is the democratic science. It bestows upon the poorest what once were the gifts of kings." It is the joyous science and contributes most to the pleasures of life. "Chemistry is a practical science. None touches everyday life at more points except its sister science, physics, between which and chemistry no clear boundary can be drawn. None has more avenues for profitable employment."

But read the preface and consider the possibilities of arranging a popular course of lectures in chemistry in your own community!

Earning Power of Research

SOME years ago engineers at a cotton textile plant introduced an air conveying system so that prepared fiber might be quickly and cheaply transported from one part of the immense plant to another. The system was successful until cold weather came. Then the moisture in the conveying air froze in the pipe between buildings. As the moisture froze, the fibers became attached and soon stopped the entire system. After surveying the situation the engineers concluded that the conveyor must be surrounded with steam pipes to prevent freezing. The cost was estimated at $30,000. The report was made to the president in the presence of the chemist, who required no research to understand the factors of the problem. He recommended that the fibers be conveyed in cold air drawn in from outside the building and therefore of the same relative humidity as the air around the conveyor. Although the engineers predicted it would not work, this method was tried and succeeded. The $30,000 was saved through the observation of a chemist. It pays to have one around.

BEFORE research developed accelerators for the vulcanization of rubber, two to three hours were required to complete the process. Much research still remains to be done upon organic accelerators but already results have been achieved which reduce the time to about thirty minutes. Another way of stating this is to say that with the introduction of accelerators one-third the former vulcanizing plant is required in a factory of a given size, and the capacity of the entire plant has been doubled.

Detonation Characteristics of Blends of Aromatic and Paraffin Hydrocarbons[1]

By **Thomas Midgley, Jr.,**[2] **and T. A. Boyd**[2]

GENERAL MOTORS RESEARCH CORPORATION, DAYTON, OHIO

The following paper presents the results obtained in a careful measurement of the effects of various concentrations of benzene, toluene, or xylene upon the detonation tendency of paraffin fuels in badly carbonized or high compression engines.

Most of the determinations were made on blends with kerosene, on account of its greater tendency to detonate. As a standard of comparison, use was made of paraffin fuels containing small amounts of xylidine, which, in common with other aromatic amines, exerts a powerful suppressing action on detonation.

A simple basis for determining the amount of benzene necessary to add to a paraffin fuel in order to obtain a given effect is as follows: Up to a concentration of 70 per cent by molecules, the effectiveness of benzene for suppressing detonation varies directly as the square of its molecular concentration (Fig. 3).

THE "knocking" that is so familiar in automobile engines when laboring on hills with wide open throttle has commonly been attributed to preignition. This conception, however, has been proved erroneous. The "knock" under such conditions is probably due to a detonation of part of the fuel charge, and the tendency of a fuel to detonate is a function of its chemical composition. Furthermore, the detonating tendency of a fuel of given composition and structure varies with the compression to which it is subjected, with the effectiveness with which the engine is cooled, and with the degree of carbonization in the cylinders of the engine. The tendency of a fuel to knock or detonate in a given engine is influenced also by some elements of design, such as, for example, the spark plug location.

It has been known for some time that the addition of benzene and certain other aromatic hydrocarbons to paraffin-base gasolines greatly reduces the tendency of the fuel to detonate when used in automobile engines.

The extension of the by-product coking industry in the United States during the recent war generated a capacity for the production of light oil which could only be absorbed by the use of a part of the material as a motor fuel. Since 1918, therefore, mixtures of benzene (or "motor benzene") and blending naphtha have been rather widely sold as motor fuels in this country, and at about the same price as gasoline.

Very few accurate quantitative data have been published on the effect of the blending of aromatic hydrocarbons with paraffin-base gasolines upon the tendency of the latter to knock or detonate. The primary reason why more of these fundamental data have not been obtained and made generally available is the previous lack of a means for measuring the detonating tendency of fuels with sufficient accuracy. A device has recently been developed with which the tendency of a fuel to detonate can be determined with a high degree of accuracy and reliability.[3] The purpose of this paper is to present some results obtained in the careful measurement of the effects of various concentrations of different aromatic hydrocarbons upon the detonation tendency of paraffin fuels in badly carbonized or high compression engines.

In order that the effects of aromatic hydrocarbons in as wide a range of concentrations as practicable might be measured, they were blended with kerosene for making the majority of the determinations reported in this paper. The greater tendency of kerosene than lighter paraffin hydrocarbons to detonate made it possible to determine the detonation characteristics of blends up to a concentration of 80 per cent benzene without introducing the difficulties incident to excessively high engine compressions.

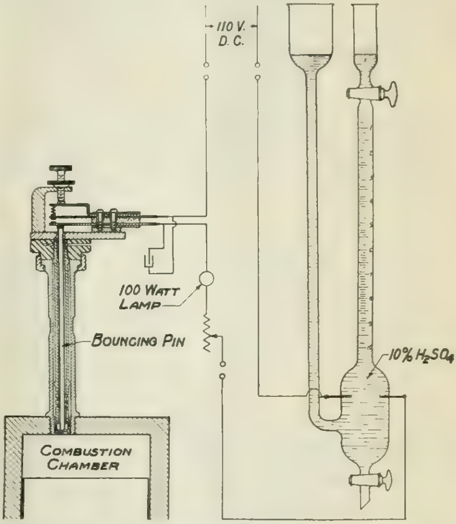

FIG. 1—APPARATUS FOR MEASUREMENT OF DETONATION BY THE BOUNCING PIN METHOD

On account of variations in motor conditions it is evident that data obtained from any particular engine are applicable in a quantitative way only to that one motor design and set of conditions. But, although widely different behavior may characterize the combustion of a given fuel in two engines, the relative behaviors of two given fuels will be comparative in whatever type of motor they may be run. Hence, in measuring the detonating tendency of any fuel it is essential that some standard fuel be used as a basis of comparison. In the tests reported herein small percentages of xylidine, in the same paraffin fuel as was used for blending with the aromatic hydrocarbons, were employed as a standard. Xylidine has the property, common to aromatic amines and considerably more marked in a number of other materials, of exerting a powerful suppressing action on detonation, when present in a fuel in percentages that are

---

[1] Presented before the Petroleum Section at the 63rd Meeting of the American Chemical Society, Birmingham, Ala., April 3 to 7, 1922.

[2] Chief and Assistant Chief of the Fuel Section of the General Motors Research Corporation, Dayton, Ohio.

[3] For a discussion of the relative merits of the various means that have been used for observing and measuring detonation in engines see Midgley and Boyd, "Methods of Measuring Detonation in Engines," *J. Soc. Automotive Eng.*, **10** (1922), 7.

Table I—Physical Data on Fuels Used in Tests

Hydrocarbon	Sp. Gr. 15° C.	Absorption in Cold H_2SO_4 Per cent	Distillation Temperatures, ° C.[1]											
			First Drop	10%	20%	30%	40%	50%	60%	70%	80%	90%	95%	Dry
Kerosene	0.816	7	186	201	207	212	217.5	222	227.5	233.5	241	253.5	268	291
Commercial gasoline	0.734	5	40	65	83.5	99	111.5	125	140	157.5	177	200	219	226
"High Test" gasoline	0.704	3	44	59	68.5	76	82.7	89.3	96	103	114	128	157	178
Benzene (90° benzene)	0.878	..	74	77.5	78.7	79.2	79.8	80.1	80.5	81.1	82	85	92.5	...
Toluene	0.860 (about)	..	107	108	108.5	108.6	108.7	108.8	108.8	108.8	108.9	109	109.2	...
Xylene	0.860 (about)	..	135	136	136.2	136.5	136.7	136.9	137.1	137.3	137.5	137.8	138.1	...

[1] The apparatus used conformed approximately to the standard of the Committee for the Standardization of Petroleum Specifications as given in their *Bulletin* 5, published by the U. S. Bureau of Mines.

relatively very small. Thus, it may be seen from Fig. 2 that 1 per cent of xylidine in kerosene is equivalent for the elimination of detonation to about 15 per cent of benzene in the same fuel. This property of the material makes it possible to convert kerosene into a fuel that will withstand very high compressions without knocking, and this with the addition of such a small percentage of xylidine that the combustion characteristics of the fuel, other than its tendency to detonate, are not materially changed.

Properties of Materials Used as Fuels

The materials used as ingredients of the various fuels that were either examined or employed as standards in the examinations were "high test" gasoline, commercial gasoline, kerosene, xylidine, benzene (90° benzene), toluene, and xylene. The xylidine employed was a commercial material, composed of the mixed xylidines. Some physical properties of the other materials are tabulated in Table I.

Apparatus

A $^3/_4$-kw. Delco-Light engine was used for making all the determinations. This is a single cylinder, air-cooled engine, directly connected to a 32-volt d. c. generator, and having a 2.5-in. bore and a 5-in. stroke. The engine was standard in every way, except that the mixing valve was bored to a larger inside diameter, that a means was provided for adjusting the spark timing, and that the compression was increased by stages from the normal ratio of 3.47 : 1 to a ratio of 5.36 : 1, by means of a series of cylinder heads which had been cut down by different amounts so as to reduce the clearance volume by corresponding stages.

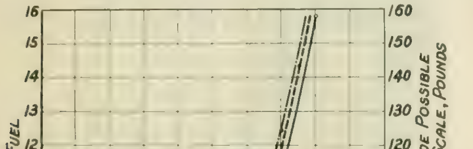

Fig. 2—Graphical Representation of Data Obtained in Determination of Detonation Characteristics of Blends of Aromatic and Paraffin Hydrocarbons
(Plotted from data in Columns 4, 5, and 7; Tables II, III, IV, and V)

The device that was employed for measuring the relative intensities of different detonations, and called the "bouncing pin" apparatus, is shown diagrammatically in Fig. 1. An essential part of this device is a combination of a bouncing pin with the standard pressure element of the Midgley Indicator.[4] This pressure element is designed to screw directly into the combustion chamber and to come flush with the inner surface of the cylinder head. The lower end of the element embodies a small piston, the upward movement of which is resisted by a heavy spring. In the original element the movement of the piston resulting from pressure changes in the combustion chamber is transmitted through a very light rod to an arm which operates to change the vertical angle of a small mirror, supported on a horizontal axis at the top of the element, in proportion to the pressure on the piston. In the bouncing pin apparatus the mirror and the shaft connecting it to the piston have been replaced by a heavy pin which rests on the piston simply by gravity. During normal combustion this pin moves up and down very slightly (only a few thousandths of an inch), owing to its following the movement of the piston resulting from normal pressure changes in the cylinder. But when detonation occurs in the combustion chamber the rod jumps upward a noticeable distance and entirely clear of the piston. The amplitude of movement of the pin varies with the intensity of detonation. It has been observed to jump as high as 1.5 in. above its normal position.

Since two successive explosions in a cylinder are rarely exactly alike, the desired degree of accuracy could not be obtained without an integration of the fluctuations of the pin over a period of time. The rest of the apparatus illustrated in Fig. 1 was arranged to accomplish this result. Contact points were held in position in an electric circuit by springs immediately above the upper end of the bouncing pin, in such a way as to be closed when the pin was thrown free of the piston. An integration of the length of time the contact points were closed was then obtained by measuring the volume of gas evolved during a 1-min. period by an electrolytic cell placed in series with the points. To the cell, which contained a 10 per cent solution of sulfuric acid in distilled water, 110 volts direct current were applied through a resistance unit, this high voltage being used to reduce polarization. Platinum electrodes were used in the cell which, as is shown in Fig. 1, was designed so that the evolved gas was automatically collected in a slender graduated tube at the top where its volume could be easily noted. Since the amount of gas evolved during a given period by one fuel was always compared with that evolved by a fuel of similar detonation characteristics that was run immediately before and after it, no correction of the volume of gas was made for

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[4] For description of this pressure element and its function see "High Speed Indicators," by Thomas Midgley, Jr., *Trans. Soc. Automotive Eng.*, 15 (1920), 317.

TABLE II—DATA OBTAINED IN DETERMINING DETONATION CHARACTERISTICS OF VARIOUS BLENDS OF BENZENE AND KEROSENE

DETERMINATION NUMBER	Compression Ratio	Spark, Degrees before T. D. C.	BENZENE-KEROSENE BLEND Benzene Per cent by Vol.	Kerosene Per cent by Vol.	DETERMINED EQUIVALENT XYLIDINE IN KEROSENE, PER CENT BY VOLUME Individual	Average
12	3.47	43	15	85	1.0	
20	3.47	43	15	85	1.0	
21	3.47	43	15	85	1.0	1.0
13	3.47	43	25	75	2.05	
15	3.47	43	25	75	1.95	
16	3.47	43	25	75	2.25	2.1
11	3.87		40	60	4.3	4.3
22	3.87	43	45	55	4.7	
23	3.87	43	45	55	4.7	4.7
28	4.59	32	55	45	7.05	
29	4.59	32	55	45	7.05	7.05
10	5.36		70	30	10.65	
37	5.36	25	70	30	11.3	
38	5.36	25	70	30	11.5	
39	5.36	25	70	30	11.4	11.2
40	5.36	25	80	20	15.8	
41	5.36	25	80	20	15.85	
42	5.36	25	80	20	15.85	15.8

TABLE III—DATA OBTAINED IN DETERMINING DETONATION CHARACTERISTICS OF VARIOUS BLENDS OF TOLUENE AND KEROSENE

DETERMINATION NUMBER	Compression Ratio	Spark, Degrees before T. D. C.	TOLUENE-KEROSENE BLEND Toluene Per cent by Vol.	Kerosene Per cent by Vol.	DETERMINED EQUIVALENT XYLIDINE IN KEROSENE, PER CENT BY VOLUME Individual	Average
17	3.47	43	20	80	1.8	1.8
14	3.47	43	25	75	2.55	2.55
24	3.87	43	45	55	5.25	
25	3.87	43	45	55	5.35	5.3
30	4.59	32	55	45	7.4	
31	4.59	32	55	45	7.15	
32	4.59	32	55	45	7.15	7.25
45	5.36	25	70	30	11.75	
46	5.36	25	70	30	11.9	11.85
43	5.36	25	75	25	14.4	14.4

TABLE IV—DATA OBTAINED IN DETERMINING DETONATION CHARACTERISTICS OF VARIOUS BLENDS OF XYLENE AND KEROSENE

DETERMINATION NUMBER	Compression Ratio	Spark, Degrees before T. D. C.	XYLENE-KEROSENE BLEND Xylene Per cent by Vol.	Kerosene Per cent by Vol.	DETERMINED EQUIVALENT XYLIDINE IN KEROSENE, PER CENT BY VOLUME Individual	Average
18	3.47	43	20	80	1.8	
19	3.47	43	20	80	2.05	1.95
26	3.87	43	45	55	6.05	
27	3.87	43	45	55	6.05	6.05
33	4.59	32	55	45	7.75	
34	4.59	32	55	45	7.80	
35	4.59	32	55	45	7.85	7.8
47	5.36	25	70	30	12.2	
48	5.36	25	70	30	12.7	12.45

TABLE V—DATA OBTAINED IN DETERMINING DETONATION CHARACTERISTICS OF BLENDS OF BENZENE AND GASOLINE

DETERMINATION NUMBER	Compression Ratio	Spark, Degrees before T. D. C.	BENZENE-GASOLINE BLEND Benzene Per cent by Vol.	Gasoline Per cent by Vol.	Designation	DETERMINED EQUIVALENT XYLIDINE IN GASOLINE, PER CENT BY VOLUME Individual	Average
59	5.36	25	50	50	Com. gasoline	5.0	
60	5.36	25	50	50	Com. gasoline	5.1	5.05
63	4.59	32	25	75	Com. gasoline	1.7	
64	4.59	32	25	75	Com. gasoline	1.85	1.8
61	5.36	25	25	75	H. T. gasoline	1.65	
62	5.36	25	25	75	H. T. gasoline	1.65	1.65

temperature or for the slight liquid pressure resulting from the design of the apparatus.

A rapid and complete change of the fuel entering the engine when desired was facilitated by the use of a special fuel system. This device consisted of two carburetor float bowls, so arranged as to be adjustable for vertical position, and two vertical glass tubes placed side by side, each connected at its bottom to one of the float bowls. Each of these tubes was connected in turn to a 3-way stopcock from which a single fuel line of small diameter ran to the engine. This arrangement permitted rapid switching from one fuel to another maintained at the proper level to give the correct amount of fuel to the engine. A mixing valve, which was standard, except that it was bored to a larger internal diameter, was used for metering the fuel to the engine; so that in changing fuels no complication was introduced from the residual fuel that remained in the float bowl of a carburetor. A means was provided for the complete draining of the part of the fuel system not in use, so as to permit the ready substitution of different fuels.

METHOD

The method of making the determinations can best be explained by giving a specific example, for which the comparison of a 45 per cent benzene–55 per cent kerosene blend with fuels composed of small percentages of xylidine in kerosene will be employed. A compression ratio of 3.87 was used, so that some detonation would occur, but which was not so violent as to cut down seriously the power of the engine or to cause it to operate in an erratic manner. The fuel under examination was put into one side of the fuel system, and the mixing valve on the engine was adjusted so as to give a maximum of detonation, which is an adjustment that lies close to the leanest possible mixture for maximum power. By trial it was found that 5 per cent of xylidine in kerosene had a very slightly lesser detonating tendency than the benzene-kerosene blend under examination. This fuel was then placed in the other side of the fuel system, and its level was adjusted so as to give the point of maximum detonation. The setting of the mixing valve was left undisturbed throughout the determination so that the compression pressure of the engine would be unchanged. A number of alternate 1-min. runs were then made with the 5 per cent xylidine in kerosene and the 45 per cent benzene–55 per cent kerosene blend, and the amount of gas evolved in the electrolytic cell during each period was recorded. The output of the generator on the plant in volts and amperes was also kept, simply as a matter of record. After from

TABLE VI—AVERAGE MOLECULAR WEIGHTS OF PARAFFIN FUELS, AND DATA ON WHICH THEY ARE BASED

FUEL	Sp. Gr. 15° C.	Average Boiling Point ° C.	FIRST NORMAL PARAFFIN HYDROCARBON BELOW AVERAGE BOILING POINT		FIRST NORMAL PARAFFIN HYDROCARBON ABOVE AVERAGE BOILING POINT		Approximate Average Molecular Weight of Fuel
			Formula	B. P.	Formula	B. P.	
"High Test" gasoline	0.704	95	C_6H_{14}	69	C_7H_{16}	98.5	98.5
Commercial gasoline	0.734	126	C_8H_{18}	125.6	C_9H_{20}	149.5	114.3
Kerosene	0.816	226	$C_{12}H_{26}$	214.5	$C_{13}H_{28}$	234	178.5

TABLE VII—RELATIONS BETWEEN AMOUNTS OF XYLIDINE AND BENZENE REQUIRED TO IMPART TO PARAFFIN FUELS LIKE COMBUSTION CHARACTERISTICS FROM THE STANDPOINT OF DETONATION

Xylidine in Paraffin Fuel by Volume Per cent	BENZENE-PARAFFIN BLEND			
	IN PERCENTAGES BY VOLUME		IN EQUIVALENT PERCENTAGES BY MOLECULES	
	Benzene	Kerosene	Benzene	Kerosene
1.0	15	85	30.0	70.0
2.1	25	75	44.8	55.2
4.2	40	60	61.8	38.2
5.9	50	50	70.8	29.2
8.2	60	40	78.5	21.5
11.2	70	30	85.0	15.0
15.8	80	20	90.5	9.5
	Benzene	Com. Gasoline	Benzene	Commercial Gasoline
0.85	15	85	23.4	76.6
1.8	25	75	36.6	63.4
3.6	40	60	53.6	46.4
5.05	50	50	63.0	37.0
	Benzene	"High Test" Gasoline	Benzene	"High Test" Gasoline
1.65	25	75	34.1	65.9

three to six runs had been made on each fuel, the 5 per cent xylidine in kerosene was replaced with 4 per cent xylidine in kerosene, and a second series of runs was made in the same manner. The amounts of gas evolved during the 1-min. runs were then averaged, and the values thus obtained for the xylidine-kerosene fuels were plotted on a coördinate chart, having as its vertical axis the amount of gas evolved per minute and as its horizontal axis the percentage of xylidine in kerosene. These two points were joined by a straight line. From the point at which this line crossed the horizontal line corresponding to the volume of gas evolved by the 45 per cent benzene–55 per cent kerosene fuel a vertical projection was made to the horizontal scale at the bottom of the chart giving per cent of xylidine in kerosene. The intersection of this projected line with the bottom scale then gave directly the percentage of xylidine in kerosene which was equivalent in its effect for the suppression of detonation to 45 per cent of benzene in kerosene.

RESULTS

The data obtained in the tests are tabulated in Tables II, III, IV, and V. Fig. 2 gives a graphical presentation of these results. The consistency of the results obtained with different concentrations of the same fuel and the close checks that were made in different determinations of the detonating characteristics of a given blend indicate that the values obtained have a high degree of accuracy. The general shape of the curves in Fig. 2 is much like what might be expected. When the aromatic concentration of an aromatic-paraffin blend is comparatively high, say 40 per cent or more, the percentage of the paraffin fuel in the blend falls off rapidly as the percentage of the aromatic constituent is increased; and so an increase in the percentage of aromatic content that is relatively small on the basis of the whole blend exerts a large influence on the detonating tendency of the fuel.

Although the amount of xylidine used as antiknock material in the kerosene in some of the tests was over 15 per cent, it was never high enough to change materially the heating value of the fuel. Practically the only effect of the addition of xylidine to the paraffin fuels was the elimination of detonation that resulted from its use. While this effect is probably not exactly a straight-line function, at least up to the higher percentages of xylidine, the amounts of the antiknock material used were never large enough to cause a great variation on account of the diluting action of the xylidine on the fuel.

It will be observed from Fig. 2 that toluene, on the basis of volume, is more effective than benzene for eliminating detonation conditions, and that xylene is, in turn, still more effective than toluene for this purpose. As may be seen from the shape of the curves in Fig. 2, the addition of only a small percentage of aromatic hydrocarbons to a paraffin fuel has but a slight effect in suppressing detonation. The curves illustrate to good advantage the reason for the observed fact that the blending of less than 20 per cent of benzene with a commercial gasoline or a naphtha exerts only a small influence toward causing the engine to give smoother operation while running on it. When benzene is blended with paraffin fuels in percentages above 20, however, its effect increases rapidly as its concentration is raised relative to the paraffin fuel. Attention has previously been called to the fact that this is due in part at least to the greater percentage reduction in the amount of the paraffin constituent present as the aromatic content is increased.

The vertical scale at the right of Fig. 2 shows approximately the increments in compression pressure of the engine that are made possible by the addition to a paraffin fuel of the corresponding percentages of xylidine given on the vertical scale to the left. From the two scales on the chart it will be observed that the addition of 1 per cent of xylidine to a fuel that just gives incipient detonation in a given engine makes it possible to raise the compression of the engine about 10 lbs., and this without any greater detonation being obtained than with the untreated fuel at the original and lower compression. The increment in compression that each per cent of xylidine makes possible can only be approximated, but the value given is based upon a number of observations made under practical operating conditions, on motors ranging from the single cylinder Delco-Light to the twelve cylinder Liberty, and over a compression range of from 50 to 160 lbs. By referring the curves of aromatic-paraffin fuels to the scale at the right an approximation may be obtained to the relative composition necessary to give smooth operation at a corresponding increase above the normal limiting or critical compression of the paraffin fuel alone.

Table VII and Fig. 3 give the relations between percentages of xylidine by volume and benzene by molecules required to impart like detonation characteristics to two representative paraffin fuels. The composition of the benzene-paraffin blends on the volume basis corresponding to the percentages of xylidine in the paraffin fuel as given in Table VII was taken from the curves in Fig. 2. The values for the average molecular weights of the paraffin fuels used in converting percentages by volume to the molecular basis were obtained by the method of Wilson and Barnard.[5] In computing the percentage composition of a blend on the molecular basis from its composition by volume, the specific gravity and the average molecular weight of each of the ingredients were employed. In view of the somewhat wide distillation range of the benzene used in the tests (Table I) a molecular weight of 79 instead of 78 was taken for benzene. The values obtained in these computations are given in Table VII.[6]

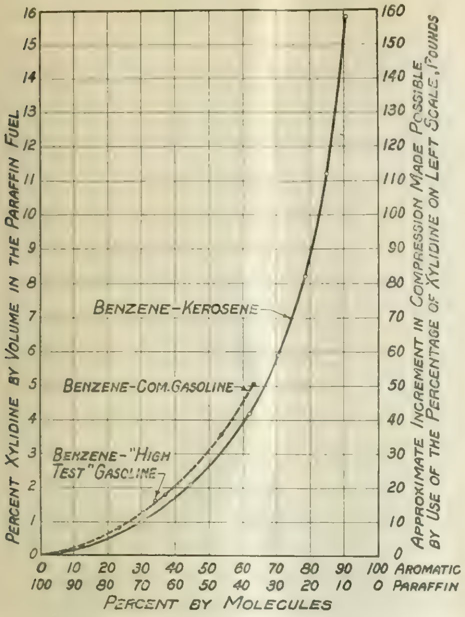

Fig. 3—Relations between Percentages of Xylidine by Volume and Benzene by Molecules Required to Impart to Paraffin Fuels Like Combustion Characteristics from Standpoint of Detonation (Plotted from data in Table VII)

The curves of Fig. 3 give a more definite basis for estimating the percentage of benzene that must be added to a paraffin fuel in order to change its detonation tendency a certain amount than is given in Fig. 2. Fig. 3 shows that on the basis of molecular concentration a somewhat lower percentage of benzene is required to produce a given effect on the critical compression of a benzene-paraffin blend, as the average molecular weight of the paraffin fuel becomes smaller. But, since a relatively large amount of benzene is required to produce a given effect on the detonation factor, the actual percentage of reduction in the amount necessary with decreasing molecular weight of the paraffin fuel is not large. A simple basis for determining the amount of benzene it is necessary to add a paraffin fuel in order to obtain a given effect is as follows: Up to a concentration of 70 per cent by molecules, the effectiveness of benzene for suppressing detonation varies directly as the square of the molecular concentration (Fig. 3).

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[5] R. E. Wilson and D. C. Barnard, 4th, "Condensation Temperatures of Gasoline- and Kerosene-Air Mixtures," This Journal, **13** (1921), 906. For this purpose the distillation data of the fuel (Table I) were arranged in the usual type of curve in which temperature is plotted on the vertical axis against per cent distilled on the horizontal axis. From this curve the percentages of the fuel distilling in each interval of 10° were obtained, and these values were plotted on a chart on which the scale of the vertical axis was in terms of per cent distilled and that of the horizontal axis was in terms of temperature. The average boiling point of the fuel was taken as the point at which a perpendicular passed through the center of gravity of the area enclosed under this differential distillation curve cut the horizontal or temperature axis. The values obtained in this way are given in Column 3 of Table VI. The approximate molecular weight of each of the paraffin fuels was computed so as to bear the same proportionate relation to the molecular weights of the hydrocarbons next above and below it in the paraffin series as the average boiling point of the fuel bore to the boiling points of the normal paraffin hydrocarbons occupying like positions with respect to it. The data used in the calculations and the value obtained for the average molecular weight of each fuel are tabulated in Table VI.

[6] It is recognized that these values are only close approximations; but, in view of the wide variations between different samples of commercial gasolines, the degree of their accuracy is as great as can have any significance when dealing with such materials. Because it is such a small factor, no account was taken in making these calculations of the slight increase in volume that occurs when aromatic and paraffin hydrocarbons are blended.

New Qualitative Test for Uranium[1]

By Harold D. Buell

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In testing slags and ores containing or supposed to contain uranium, it was found that when uranium was present zinc, added to a nitric acid solution of the material, gave a yellow deposit on the zinc. This test has never been recorded in the literature. It is very simple in manipulation and requires no special caution in regard to acid strength and temperature.

A nitric acid solution of the sample is prepared. A large excess of acid is to be avoided because the reaction may become so violent as to boil out of the test tube and an unnecessary amount of zinc will be used up. An excess of granulated zinc is added to the solution and the reaction is allowed to proceed until the acid is spent, when a yellow deposit appears on the zinc. If the reaction is too violent the acid may be diluted; if too slow, more acid may be added. The yellow color develops more rapidly as the concentration of uranium is increased, but always appears when the reaction completely stops.

The same yellow deposit was obtained from an aqueous solution of pure uranyl nitrate crystals, with no free acid present. The color did not develop, however, for two days, and the aqueous solution was acid to litmus as a result of hydrolysis.

In a solution of pure uranyl nitrate crystals with enough free nitric acid to start reaction with the zinc, it was possible to detect 0.88 mg. of uranium per cc. of solution. By concentration of the solution a more vivid color was obtained.

Gold, platinum, thorium, lead, tungsten, titanium, chromium, mercury, and copper do not interfere with the test. Iron and vanadium interfere only when present in large quantities. In the latter case, the spent liquid is removed as soon as action has ceased, and the zinc and the deposit are treated with enough nitric acid to start reaction. The deposit dissolves, but reappears when the acid is again exhausted, and vanadium and iron remain in solution.

The test is not applicable in the presence of sulfuric or hydrochloric acids, when a black deposit is obtained. The yellow deposit appears only in an oxidizing solution of nitric acid, for uranyl salts are readily reduced to uranous salts by nascent hydrogen. This should, however, serve as a preliminary test to indicate the presence of uranium at the beginning of an analysis, rather than as part of a systematic scheme of qualitative separation.

From the literature, it appears that the deposit is $UO_3 . 2H_2O$. This is the only oxide which corresponds in color to the deposit obtained.

[1] Received February 10, 1922.

Carburetor Adjustment by Gas Analysis[1,2]

By A. C. Fieldner[3] and G. W. Jones[4]

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The following paper records experimental work on the determination of carbon dioxide in exhaust gas, which has a direct bearing on carburetor adjustment.

The per cent carbon dioxide in the exhaust gas bears a direct relation to the completeness of combustion and air-fuel ratio.

Curves are given showing the carbon dioxide percentage relation to air-fuel ratio and also to completeness of combustion, both by laboratory and road tests.

Characteristic curves are given of two types of carburetors the results of which were plotted from road tests, showing how the air-fuel ratio changes with change of mixture rate through carburetor.

Procedure for sampling exhaust gases while adjusting carburetors on the road are given and a portable carbon dioxide indicator is described.

Examples of carburetor adjustment by gas analysis are given.

Tests made by the Bureau of Mines on a large number of motor vehicles, to determine the amount and composition of the exhaust gases produced under varying operating conditions, have shown that the average automobile and truck as used in service waste from 20 to 30 per cent of gasoline by incomplete combustion.[5] The average driver uses a rich mixture, which does not contain sufficient air to burn the gasoline completely. In these road tests the average ratio of pounds of air to gasoline was found to be approximately 12.5 to 1. Gasoline as used at the present time requires approximately 15 lbs. of air for complete combustion. Less than 15 lbs. of air causes the appearance of carbon monoxide, hydrogen, methane, and very small quantities of unsaturated hydrocarbons (0.1 per cent or less in most cases) in the exhaust gas.

The heat losses due to combustibles in the exhaust gases of the motor vehicles tested average for all tests approximately 30 per cent of the heat value of the gasoline used. In some instances this heat loss was over 50 per cent. At least 50 per cent of this could have been prevented by correct carburetor adjustment. Gas analysis is a positive method for determining the completeness of combustion and thus affords a ready means of adjusting the carburetor for maximum economy of gasoline. As shown by the curves and tests that follow, the carbon dioxide percentage of the exhaust gas gives directly the air-fuel ratio of the gas mixture entering the engine and percentage of completeness of combustion that has taken place.

Derivation of Air-Fuel Ratio and Per cent Completeness of Combustion Curves

The air-fuel ratio for maximum power at full load extends from about 11 : 1 on the rich side to 15 : 1 on the lean side. These results were obtained from block tests with a 19.6 h. p. Lycoming engine at a speed of 1000 r. p. m. The inlet air temperature varied from 89° to 101° F. and the cooling water was kept at 150° F. It is seen from Fig. 1 that the maximum power range decreases as the load is decreased and is from 11.5 : 1 to 14 : 1 at the lowest loads shown. Berry[6] and others have obtained curves of a similar nature which were based on actually measuring the air and gasoline supplies instead of on exhaust gas analysis. The air-fuel ratios for the above curve were obtained by calculation from a complete analysis of the exhaust gas and the carbon content of the gasoline used.

The following formula was used for computing the air-fuel ratio:

$$\text{Lbs. of air per lb. of fuel} = \frac{a \times b \times 0.0764}{0.0317\,(c + d + e) \times 0.791}$$

where a = percentage of carbon in fuel.
b = percentage of nitrogen by volume in exhaust gas.
c = percentage of carbon dioxide by volume in exhaust gas.
d = percentage of carbon monoxide by volume in exhaust gas.
e = percentage of methane by volume in exhaust gas.
0.0764 = wt. of 1 cu. ft. of air at 60° F. and 29.92 in. Hg.
0.0317 = wt. of carbon in 1 cu. ft. of CO_2, CO or CH_4 at 60° F. and 29.92 in. Hg.
0.791 = percentage of nitrogen in normal air.

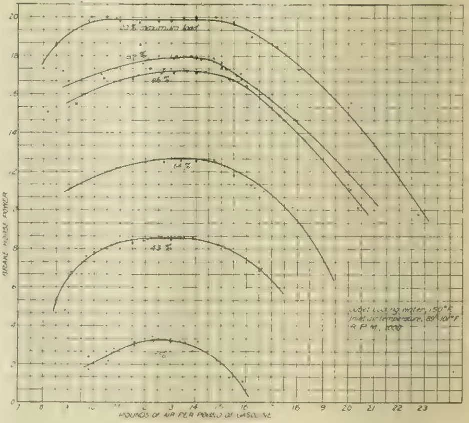

Fig. 1

Fig. 2 gives the brake thermal efficiencies obtained under the same conditions as given for the tests shown in Fig. 1. The curve shows that at wide open throttle positions maximum efficiency is obtained at an air-fuel ratio of 16.5 to 17.5 : 1, while at lighter loads the value decreases to around

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[1] Presented before the Division of Industrial and Engineering Chemistry, at the 63rd Meeting of the American Chemical Society, Birmingham, Ala., April 3 to 7, 1922.

[2] Published by permission of the Director, U. S. Bureau of Mines.

[3] Supervising Chemist, Pittsburgh Experiment Station, U. S. Bureau of Mines.

[4] Assistant Chemist, Pittsburgh Experiment Station, U. S. Bureau of Mines.

[5] A. C. Fieldner, A. A. Straub and G. W. Jones, "Gasoline Losses Due to Incomplete Combustion in Motor Vehicles," This Journal, **13** (1921), 51; *J. Soc. Automotive Eng.*, **8** (1921), 295; *Bur. Mines, Repts. Investigation*, **2225**.

[6] O. C. Berry, "Mixture Requirements of Automobile Engines," *J. Soc. Automotive Eng.*, **5** (1919), 364.

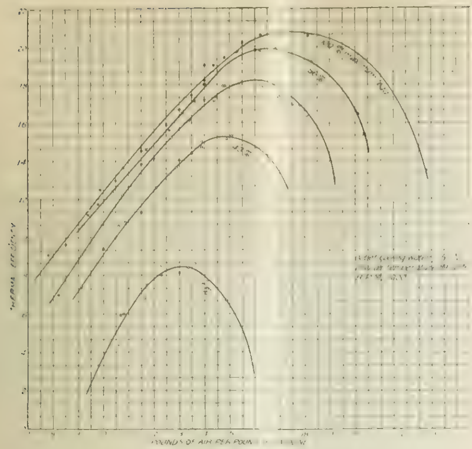

FIG. 2

13.5 : 1. Thermal efficiency is a measure of the relative mileage which may be obtained from a given quantity of fuel. To obtain high mileage the carburetor adjustment should be at a higher air-fuel ratio than that for maximum power. Power must be sacrificed to some degree in securing the greatest mileage. However, an air-fuel ratio may be chosen which will give reasonably good economy of gasoline and at the same time not sacrifice power and flexibility appreciably. Several cars tested by the Bureau showed that an air-fuel ratio of 13.7 to 14.7 : 1 can be obtained with flexible and easy operation. Each particular type of car has a maximum air-fuel ratio at which it can be operated satisfactorily. The temperature of the intake air, type of carburetor, design of the manifold, velocity of the air-fuel mixture, and turbulence in the engine govern the leanest mixture which may be used.

The relation of the air-fuel ratio to the percentage of carbon dioxide in the exhaust gas is shown in Fig. 3. This curve was obtained from laboratory block tests with only one type of gasoline. The region for maximum power, perfect combustion, and limit of maximum thermal efficiency are given as found by Figs. 1 and 2. The perfect combustion line is the theoretical ratios of air to gasoline for complete combustion found by analysis of the gasoline.

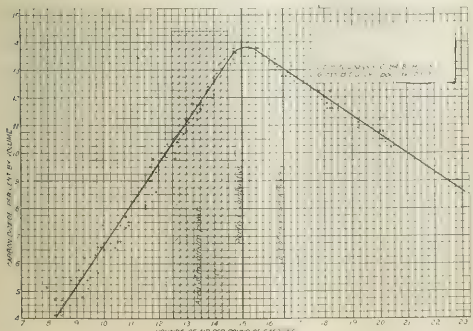

FIG. 3

Fig. 4 shows a curve obtained by plotting the carbon dioxide percentages and air-fuel ratios obtained in road tests under different conditions of operation, using different types of motor vehicles and many different grades of gasoline. It may therefore be taken as an average curve for the present-day grade of gasoline and may serve as a basis for carburetor adjustment by gas analysis. Most of the points occur at air-fuel ratios for rich adjustments. This curve follows closely the curve obtained from the laboratory block tests to the point for complete combustion.

By determining carbon dioxide in the exhaust gas the air-fuel ratio can be read from the curves and the carburetor may be adjusted accordingly.

RELATION BETWEEN PER CENT COMPLETENESS OF COMBUSTION AND PER CENT CARBON DIOXIDE IN THE EXHAUST GAS

The exhaust gas from different gasolines should contain from 14 to 14.5 per cent carbon dioxide at complete combustion of a theoretically correct mixture with air (without excess of either gasoline or air). As the combustion becomes less complete or the air is supplied in excess of that required, the percentage of carbon dioxide decreases proportionately. It is therefore possible to construct curves showing the relation between the percentage carbon dioxide and completeness of combustion. These curves may then be used in estimating the completeness of combustion from a carbon dioxide determination in the same manner as the power plant engineer checks up the efficiency of combustion in a boiler. Fig. 5 shows such a curve, the points of which were taken from tests made with 53 trucks of 1.5- to 5-ton capacity and tested at 10 mi. per hr. up a 3 per cent grade under summer conditions. The curve shows at a glance the wide range of combustion efficiency found with different trucks operated under the same conditions. In some cases about 45 per cent of the heat value of the gasoline passes out in the exhaust as a result of rich carburetor adjustment.

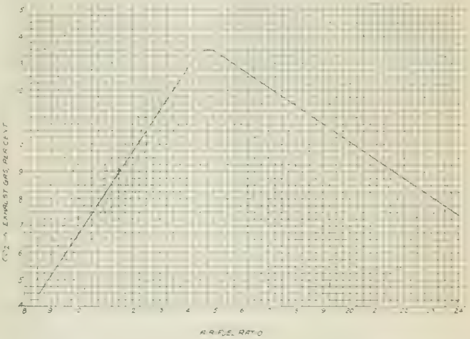

FIG. 4—SHOWING RELATION BETWEEN CO_2 PER CENT IN EXHAUST GAS AND AIR-FUEL RATIO POINTS ON CURVE TAKEN FROM TESTS UNDER ACTUAL ROAD CONDITIONS MADE ON 101 MOTOR VEHICLES USING DIFFERENT BRANDS OF GASOLINE

The percentage completeness of combustion of these tests was calculated by the following formula, making use of the exhaust gas analysis and ultimate analysis of the fuel:

CALCULATIONS FOR DETERMINING COMPLETENESS OF COMBUSTION

From the ultimate analysis of the gasoline by weight:

$$\frac{\text{Per cent hydrogen} \times 0.5}{\text{Per cent carbon} \times 0.0833} = \text{ratio of water vapor to carbon dioxide by volume on complete combustion} = A.$$

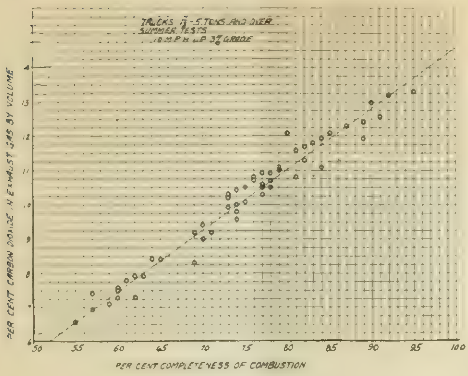

Fig. 5

Taking the heat of combustion of carbon as 14,540 B. t. u. and that of hydrogen as 62,000 B. t. u.,

$$\frac{14{,}540 \times \text{per cent carbon}}{(14{,}540 \times \text{per cent carbon}) + 62{,}000 \times \text{hydrogen}} = \text{per cent heat units due to carbon} = B.$$

$$\frac{62{,}000 \times \text{per cent hydrogen}}{14{,}540 \times \text{per cent carbon} + 62{,}000 \times \text{per cent hydrogen}} = \text{per cent heat units due to hydrogen} = C.$$

From gas analysis by volume:

$$\text{Per cent } CO_2 + 2CO + \text{per cent } CH_4 = \text{volume carbon containing gases} = D.$$

$$\frac{\text{Per cent } CO_2 + (0.3 \times \text{per cent } CO)}{\text{Per cent } CO_2 + \text{per cent } CO + \text{per cent } CH_4} = \text{completeness of combustion of carbon} = E.$$

$D \times A$ = equivalent volume of water vapor formed on complete combustion.

$$1 - \frac{\text{per cent } H_2 + \text{per cent } CH_4}{D \times A} = \text{completeness of combustion of hydrogen} = F.$$

Hence, completeness of combustion of gasoline $= (B \times E) + C(C \times F)$.

The factors A, B, and C are practically constant for any given grade of gasoline. This greatly simplifies the calculations when a series of tests are made.

Sampling Exhaust Gases

The exhaust gas should be sampled from the exhaust pipe at a point between the engine and the muffler. The location should be as near the muffler as possible in order that the gases from the different cylinders may have the maximum mixing before sampling.

If samples are taken from the muffler they may become contaminated with air due to leakage, and in some types of motor vehicles the pressure may not be sufficient to cause the exhaust gas to flow through the sampling arrangement.

Carburetor Adjustment

To adjust a carburetor by gas analysis, tests should be made on the road under the different conditions under which the automobile or truck is driven by the operator. The automobile should be run until it is thoroughly warmed up and operating satisfactorily and then tested at a given speed, say 20 mi. per hr. on the level, by taking exhaust gas samples and analyzing for carbon dioxide content. By referring to Fig. 4 the air-fuel ratio can be obtained. Should the percentage of carbon dioxide be low, the carburetor is given a slightly leaner adjustment and again tested, and a record is kept of the carbon dioxide percentage and carburetor adjustment for each test. If the carburetor has two or more independent adjustments they should be investigated separately to determine the effect of each adjustment at the given speed. When the highest carbon dioxide percentage consistent with flexible operation at this speed has been obtained, the automobile should be tested at other speeds and a record kept of the carbon dioxide percentages and carburetor settings. Then, by plotting the carbon dioxide percentages found at the different speeds, the carburetor setting giving the highest average carbon dioxide percentage at the different speeds and also flexible operation should be chosen as the best adjustment.

If a characteristic curve of the carburetor being tested is known, only one test is necessary to adjust for most conditions under which the automobile may be used. Fig. 6 shows such a curve of the metering pin type of carburetor and gives the air-fuel ratio which the carburetor meters into the engine at the different mixture rates passing through the carburetor. The curve was obtained by averaging the tests from three automobiles using this type of carburetor and shows that as the velocity of gas mixture increases the air-fuel ratio likewise increases to a certain point, above which it remains fairly constant. This particular carburetor gives the needed rich mixture at low velocities for flexibility in driving at low speeds and then increases the air ratio as the speed increases, which permits economy of gasoline.

The tests made on these three automobiles gave low percentages of carbon monoxide, good mileage, and high values for completeness of combustion. The carbon dioxide percentage in the exhaust gas is over 12 per cent at mixture rates over 9 cu. ft. per min. In adjusting a carburetor of this type it is necessary, having the characteristic curve as shown in Fig. 6, only to test the car at one speed, say at 20 mi. per hr. on level grade, and to adjust the carburetor to give a carbon dioxide percentage of 12.5, as shown in Fig. 6. At low speeds and idling positions the mixture is rich enough to give good operation.

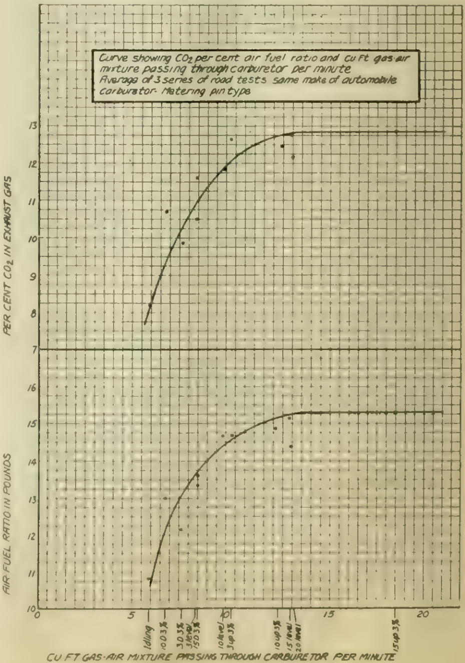

Fig. 6

Fig. 7 gives a similar curve showing the characteristics of a surface evaporation type of carburetor. As the air velocity increases, the mixture becomes richer, while for economy the air-fuel ratio should go the other way. At low velocity the mixture is leaner; it should be richer for good idling qualities and light loads. Under the usual driving conditions the carbon dioxide percentage cannot be increased so high as that shown in Fig. 6, for the mixture would be too lean at low speeds to give satisfactory operation. Until curves similar to the above are obtained by actual road tests for each type or class of carburetor definite methods or values for percentage of carbon dioxide, which the exhaust gas should contain, cannot be given. The two above curves are given as examples to show the types of curve, one of which gives very good mileage, completeness of combustion, operation, and carbon dioxide analysis, and the other in which the carburetor functions in the wrong direction and makes it very difficult to get a good combustion efficiency.

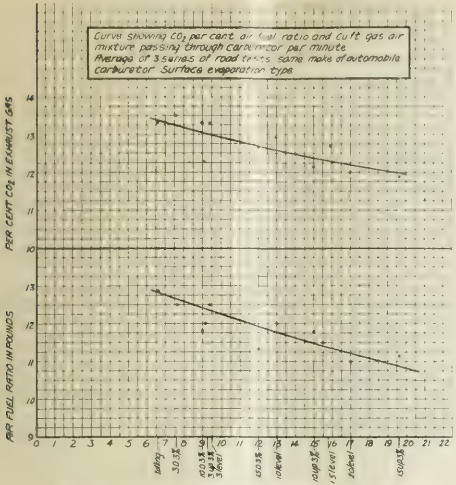

Fig. 7

Carbon Dioxide Indicator

A carbon dioxide indicator for adjusting carburetors on the road has been devised, by means of which the exhaust gas sample is taken directly into the buret while the car is in motion and the carbon dioxide percentage is determined while stopping until the analysis is made, or on smooth roads while the car is in motion.

The indicator was designed to be as nearly leak-proof as possible and easily and speedily operated by the layman, yet accurate within the limits of sampling the gases.

Two minutes are required to sample and analyze the gas, a marked saving in time over the usual method. The time is so short that temperature changes do not affect the result appreciably.

Tar and soot in the exhaust gas do not clog the indicator because its only stopcock has a large (6-mm. bore) opening.

The only special part of the indicator is the buret, which is provided with a rugged stopcock having large openings in the plug and connecting branches to give an easy passage for the gas. Below the stopcock is the body of the buret, which has a glass jet extending nearly to the top of the bulb as shown in Fig. 8. In the upper end of this jet are several very fine holes evenly spaced about the top at an angle of 45° with the horizontal. From these holes dilute caustic soda solution is forced out of the jet for absorbing the carbon dioxide. From the bulb of the buret extends a slender tube of the proper size to cover the carbon dioxide percentages which may be found in the usual type of gases. For exhaust gases the scale extends from 5 to 14.5 per cent. For gas which may have a higher carbon dioxide content a tube slightly larger in diameter must be used.

C and H are wide-mouth bottles of 500-cc. capacity; J is a 250-cc. wide-mouth bottle. The buret and bottles with capillary connections and rubber tubing are mounted on a suitable stand, as shown in Fig. 9.

Bottle C is filled to the point indicated in the figure with 5 per cent sulfuric acid solution. The height may vary somewhat without appreciably affecting the accuracy of analysis, but sufficient solution must be present to form a seal for the lower end of the buret when the buret is filled with liquid and ready for taking a sample. The dilute acid solution is introduced into C by removing the small glass plug B and slipping a piece of hollow glass tubing into the rubber connection at B the other end of which dips into the reserve supply of solution. By suction on tube A, the acid is drawn into bottle C until filled to the proper height. The glass tubing is then removed and the glass plug reinserted.

Bottle J is filled with a 10 per cent caustic soda solution by removing glass plug M and inserting a small funnel in its place.

Enough water is poured into bottle H to form a water seal with the rubber tube extending into the bottle from G. After the caustic soda solution is blown to the tip of jet K by blowing on rubber tube L and opening pinch clamp T the indicator is ready for use.

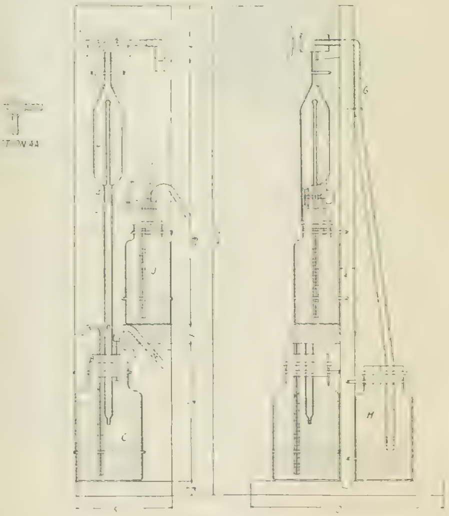

Fig. 8

To make a determination cock E is turned to the position as shown in section A-A (Fig. 8), and by blowing in rubber tube A, liquid is forced into the buret; when the liquid reaches cock E, it is turned 180°, thus filling the buret completely with the liquid. Fig. 10 shows the arrangement for sampling the exhaust gas from a motor vehicle while in motion. The gas coming through the exhaust tube causes a stream of gas

TABLE I—TESTS ON FORD TOURING CAR

Weather—clear; temperature—68° F.; humidity—65.
All tests made over a 1-mi. course and up an average 3 per cent grade.
Course was macadamized and in good condition.

Test No.	Mi. per Hr.	Gasoline Used Cc.	Exhaust Gas Analysis CO_2	O_2	CO	CH_4	H_2	Tested	Mi. per Gal.	Increase Per cent
1	15.1	278	7.4	2.1	10.3	0.2	5.3	B	13.6	....
2	15.6	222	11.5	2.0	4.1	0.0	1.8	A	17.0	23.5
3	19.4	235	11.0	2.0	4.8	0.0	2.4	A	16.0	....
4	18.8	290	7.2	2.4	11.0	0.0	6.4	B	13.0	23.1

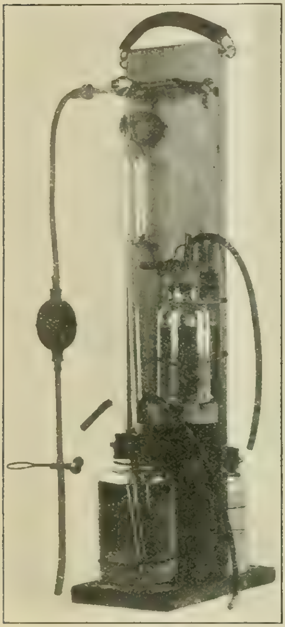
FIG. 9

to pass through cock E and out through the water seal H. When the automobile is operating at the desired speed a sample is taken into the indicator by turning cock E to the left 90°, thus allowing the liquid in the buret to fall and pull in a sample of gas. The exhaust pressure is sufficient to force the gas out through the bottom of the buret into bottle C. Cock E is then turned 90° to the right and the gas in the buret allowed to stand 30 sec. to permit the gas to come to the surrounding temperature and allow the buret to drain. Allowing the gas to stand and cool draws some liquid from C into the bottom of the buret on account of contraction of the gas.

TABLE II—TESTS MADE ON SIX-CYLINDER CAR

Weather—clear; temperature—65° F.; humidity—60.
All tests made over a 1-mi. course and up an average 3 per cent grade.
Course macadamized and in good condition.

Test No.	Mi. per Hr.	Gasoline Used Cc.	Exhaust Gas Analysis CO_2	O_2	CO	CH_4	H_2	Air-Fuel Ratio	Mi. per Gal.	Increase Per cent
1	15	403	8.7	2.0	...	...	...	11.4	9.4	...
2	15	370	9.7	2.2	6.8	0.0	3.2	12.0	10.2	8.8
3	15	318	12.6	2.4	2.8	0.0	0.6	13.8	11.9	26.6
4	20	418	8.7	1.6	...	...	...	11.4	9.0	...
5	20	345	11.7	1.8	...	...	...	13.4	10.9	21.2

At the end of 30 sec. cock E is turned 90° to the left, and enough gas is allowed to enter to bring the gas volume exactly to the bottom of the buret. E is then turned 90° to the right. There is now a definite measured volume of gas in the buret at the temperature of the indicator. Caustic soda is forced into the buret from the jet K by blowing on L and at the same time opening pinch clamp T. Six separate small charges or more of the caustic soda solution are forced into the buret in succession, allowing sufficient time for the caustic solution to drain down the buret before the next charge is introduced. An interval of 10 sec. has been found sufficient. The highest point reached by the solution is the correct reading.

The indicator is made ready for another analysis by again blowing into tube A and filling the buret as previously directed. The dilute sulfuric acid solution in C when forced into the buret neutralizes the caustic soda solution each time so there is no absorption of carbon dioxide when the sample is being taken and brought to the surrounding temperature.

A small amount of solution is blown each time over into bottle H when the buret is filled so that the liquid height in C is kept approximately at the same level in C.

A few drops of phenolphthalein solution are added to the caustic soda solution which turns the solution in C pink when it has become exhausted.

The bottle J holds sufficient caustic solution to make from 25 to 35 determinations, depending on how economically the solution is used.

It is very necessary when the first charge of caustic soda solution is blown into the buret that only enough pressure is applied barely to cause the caustic solution to run down the sides of the jet, otherwise a small bubble of gas will be blown out of the bottom of the buret and this in turn will give too large a percentage indication of carbon dioxide.

Laboratory tests show the indicator to be accurate to 0.2 per cent with carbon dioxide contents of 14 per cent and more accurate at lower percentages. On actual road tests with automobiles where conditions are very unfavorable, as a result of temperature changes and the jolting action of the machine in motion, the error may be as high as 0.5 per cent. This, however, is within the accuracy of taking samples under these conditions.

The following samples show the gain in mileage which can be obtained by proper carburetor adjustment.

Table I shows tests made on a Ford automobile. The driver had used the adjustment shown in test for some time. By adjusting the carburetor to give a higher carbon dioxide percentage, as shown in Test 2, the mileage was increased 23.5 per cent.

Table II shows results obtained with a six-cylinder automobile. By adjusting the carburetor to give a carbon dioxide percentage as shown in Test 3 a marked increase in mileage was accomplished.

TABLE III—TESTS MADE ON AN EIGHT-CYLINDER AUTOMOBILE

Test No.	Mi. per Hr.	Gasoline Used	Mi. per Gal.	Exhaust Gas Analysis CO_2	O_2	CO	H_2	CH_4	Carburetor Adjustment
10	14.7	570	6.6	8.9	...	...	...	...	A at 3.5 B 1/4 turn to right
1	15.0	473	8.0	11.7	0.7	3.1	1.0	0.5	A 1.3 turns to left B same as Test 10
2	15.0	453	8.3	11.8	1.0	2.2	0.6	0.5	A 1.5 turns to left B same as Test 10
3	14.8	453	8.3	11.9	1.1	2.1	0.7	0.4	A 1.7 turns to left B same as Test 10
4	14.8	435	8.7	12.2	1.2	1.6	0.3	0.4	A same as Test 3 B 2 turns to left
5	14.6	422	8.9	12.3	1.4	1.4	0.2	0.4	A 1.9 turns to left B same as Test 4
6	15.0	422	8.9	12.4	1.6	1.0	0.0	0.4	A 2.1 turns to left B same as Test 5
7	15.0	443	8.5	11.6	2.8	1.2	0.0	0.3	

A = Air valve adjustment; B = Gasoline adjustment.
Test 10 gives the adjustment of carburetor that had been used previous to tests.
The carburetor was then adjusted by exhaust gas analysis to give as high CO_2 content as possible and still be easy to operate.
Tests were then made over the 1-mi. course and up a 3 per cent grade to determine the maximum efficiency which might be obtained. Tests 1 to 6 give the results of these tests. The car was afterwards operated at adjustment as given under Test 4.

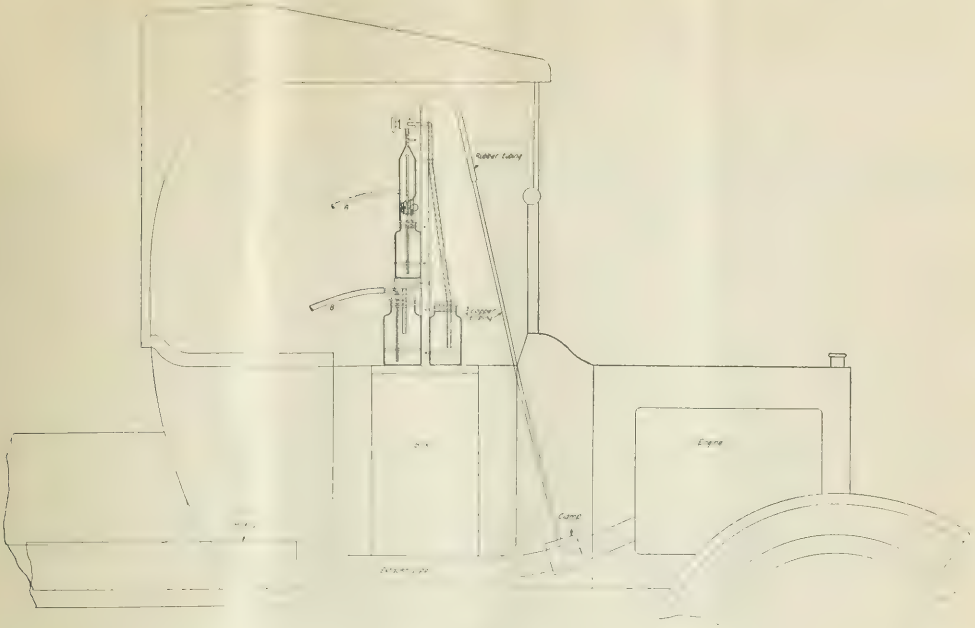

Fig. 10

Table III shows results obtained with an eight-cylinder automobile. The adjustment which has been used previous to the tests is given by Test 10. By readjusting the carburetor the mileage was increased as shown. The adjustment shown by Test 6 was found to be too lean when tested at low speed on hills and the carburetor was changed back to the setting given by Test 4 and operated at that adjustment satisfactorily.

Table IV—Effect of Carburetor Adjustment on Gasoline Consumption and Exhaust Gas Analysis on Loaded 3.5-Ton Truck

Truck equipped with a 4-cylinder, 3³/₄-in. bore × 5³/₄-in. stroke L head motor, having a White carburetor containing low and high speed nozzles of fixed size. The carburetor was not heated, the inlet air to carburetor was partly heated, and portion of the intake manifold is cast in cylinder block. The total weight of loaded truck was 8.55 tons. In was geared 13.3 to 1 in high gear and governed for maximum speed of 15 mi. per hr. Tests were conducted at 15 and 10 mi. per hr. up 3 per cent grade and on level grade, of dry pavement. Choke on carburetor air was left wide open on all tests which were conducted with gasoline 57.4° Bé., distillation 10 per cent—198° F.; 50 per cent—262° F.; dry—433° F.; average 275° F.

Carb. Diam. Low In.	Setting Nozzles High In.	R. P. M. Motor	Gasoline Consumption Gal. per Mi.	Gasoline Consumption Mi. per Gal.	Exhaust Gas Analysis, Per cent by Volume CO_2	O_2	CO	CH_4	H_2	N_2	Lb. Air per Lb. Gasoline	Per cent Completeness of Combustion
Results of tests at 15 mi. per hr. up 3 per cent grade												
0.032	0.032	1530	0.2871	3.48	10.8	0.4	5.1	0.8	1.5	81.4	12.6	78
0.032	0.035	1560	0.2741	3.65	11.6	0.3	4.5	0.4	1.7	81.5	12.7	82
0.033	0.038	1577	0.2805	3.57	10.4	1.3	4.6	0.9	1.5	81.3	13.2	77
0.033	0.040	1547	0.3373	2.96	9.0	0.5	7.9	0.6	3.7	78.3	11.5	69
0.037	0.046	1734	0.4679	2.14	5.8	1.0	13.4	1.4	7.8	70.6	8.8	48
Results of tests at 10 mi. per hr. up 3 per cent grade												
0.032	0.032	1096	0.3007	3.33	10.9	0.5	4.6	0.7	1.5	81.8	13.0	79
0.032	0.035	1067	0.2780	3.60	11.9	0.7	3.1	0.6	1.0	82.7	13.7	84
0.033	0.038	1090	0.2871	3.48	10.8	1.0	4.5	0.7	1.8	81.2	13.1	79
0.033	0.040	1117	0.3060	3.27	10.0	0.4	6.4	0.6	3.5	79.1	12.0	75
0.037	0.046	[1]	0.3770	1.99	5.9	1.3	12.5	1.8	6.2	72.3	9.2	51
Results of tests at 15 mi. per hr. level grade												
0.032	0.032	1655	0.1780	5.61	11.0	0.5	5.3	0.5	1.9	80.8	12.4	79
0.032	0.035	1642	0.1756	5.69	11.6	0.4	3.8	0.6	1.4	82.2	13.3	82
0.033	0.038	1662	0.1770	5.65	10.9	1.1	4.1	0.5	1.4	82.0	13.6	82
0.033	0.040	1669	0.1907	5.24	9.3	0.8	7.7	0.8	3.7	77.7	11.3	68
0.037	0.046	1642	0.2928	3.42	5.9	1.5	12.7	1.8	5.7	73.0	9.5	51
Results of tests at 10 mi. per hr. level grade												
0.032	0.032	1156	0.1727	5.78	11.0	0.6	4.7	0.7	1.6	81.4	12.8	79
0.032	0.035	1143	0.1727	5.78	12.3	0.6	2.7	0.7	0.7	83.0	13.6	85
0.033	0.038	1143	0.1743	5.73	11.5	1.6	3.7	0.9	1.0	81.3	13.0	81
0.033	0.040	1130	0.1805	5.54	9.5	0.8	6.9	1.0	3.0	78.8	11.7	69
0.037	0.046	1133	0.3001	3.33	5.4	3.5	10.7	2.6	4.2	73.6	10.2	49

[1] Changed gears.

Remarks

The mixture was not lean enough with any adjustment to decrease power sufficiently so that the truck would not meet conditions of tests. The motor did not backfire on any test after becoming thoroughly warmed, with air choke wide open. On tests with 0.032-in.–0.032-in. nozzles in carburetor (smallest used), the truck did not possess the flexibility in operation it did with other adjustment, not being as sensitive to throttle changes.

With 0.037-in.–0.046-in. nozzles in carburetor the mixture was too rich and the motor did not develop its normal power. With this adjustment the truck would not ascend 3 per cent grade at 10 mi. per hr. in fourth gear; the last part of this test was run in third gear.

Nozzles 0.033 in.–0.040 in. are supplied by manufacturers as standard for this truck for the Pittsburgh district.

Table IV shows tests made on a loaded 3.5-ton truck in which the carburetor was of the fixed jet type. Different jets were tested under the conditions given in the table. A marked saving of gasoline is possible by choosing the proper jets to give better combustion without losing power.

Table V shows tests made on a 5-ton loaded truck equipped with a carburetor having adjustable and low speed jets.

Table VI shows tests made on a 5-ton loaded truck equipped with the jets, one for idling and one for high speeds.

TABLE V—EFFECT OF CARBURETOR ADJUSTMENT ON GASOLINE CONSUMPTION AND EXHAUST GAS ANALYSIS OF LOADED 5-TON TRUCK

Truck was equipped with a 4-cylinder 5-in. bore × 6-in. stroke L head motor having a Zenith carburetor containing one nozzle for idling and lower speeds, and a main and compensating nozzle for high speeds. The size of the low and high speed nozzles for different tests were changed. The carburetor was not heated; inlet air was partly heated; and a very small portion of the intake manifold was cast in the cylinder block. The total weight of the truck loaded was 11.8 tons. It was geared 10.5 to 1 in high gear and governed for a maximum speed of 12 mi. per hr. Tests were conducted at speeds of 10 and 6 mi. per hr. up 3 per cent grade on dry asphalt pavement. Choke on carburetor air was left wide open on all tests which were conducted with gasoline 57.4° Bé.; distillation 10 per cent—198° F.; 50 per cent—262° F.; dry—433° F.; average 275° F.

Carb. Size Low	Setting Nozzles High	R. P. M. Motor	Gasoline Consumption Gal. per Mi.	Gasoline Consumption Mi. per Gal.	Exhaust Gas Analysis, Per cent by Volume CO_2	O_2	CO	CH_4	H_2	N_2	Lb. Air per Lb. Gasoline	Per cent Completeness of Combustion
Results of tests at 10 mi. per hr. up 3 per cent grade												
120	130	966	0.3207	3.12	12.4	1.1	2.0	0.7	0.5	83.3	15.0	87
125	140	964	0.3738	2.67	11.9	0.2	4.1	0.7	1.4	81.7	13.3	81
130	145	950	0.3675	2.72	9.3	0.6	6.9	0.9	2.9	79.4	12.6	70
135	150	975	0.4089	2.44	8.8	0.4	8.4	0.7	3.5	78.2	11.9	67
Results of tests at 6 mi. per hr. up 3 per cent grade												
120	130	586	0.3809	2.62	9.7	0.3	6.7	0.8	3.0	79.5	12.6	71
125	140	456	0.4445	2.25	8.1	0.4	9.4	0.6	4.7	76.8	11.5	65
130	145	548	0.4517	2.21	7.1	0.4	11.1	0.7	5.6	75.1	10.8	60
135	150	514	0.5254	1.90	6.2	0.4	12.8	1.0	7.2	72.4	9.8	53

REMARKS

The oil was carried high in crank case on these tests as it was considered somewhat light for the motor. This caused the exhaust to be slightly smoky. The nozzles 125–140 are supplied by manufacturers as standard for Pittsburgh district for this truck.

TABLE VI—EFFECT OF CARBURETOR ADJUSTMENT ON GASOLINE CONSUMPTION AND EXHAUST GAS ANALYSIS OF LOADED 5-TON TRUCK

Truck was equipped with a 4-cylinder 5-in. bore × 6-in. stroke L head motor having a Stromberg Model G 3 carburetor with adjustable low and high speed nozzles. The carburetor was not heated; inlet air was partly heated; and a very small portion of the intake manifold was cast in the cylinder block. The total weight of the truck loaded was 11.8 tons. It was geared 10.5 to 1 in high gear and governed for a maximum speed of 12 mi. per hr. Tests were conducted at speeds of 10 and 6 mi. per hr. up 3 per cent grade on dry asphalt pavement. Choke on carburetor air was left wide open on all tests which were conducted with gasoline 57.4° Bé.; distillation 10 per cent—198° F.; 50 per cent—262° F.; dry—433° F.; average 275° F.

Carb. Turns Low	Setting Nozzles High	R. P. M. Motor	Gasoline Consumption Gal. per Mi.	Gasoline Consumption Mi. per Gal.	Exhaust Gas Analysis, Per cent by Volume CO_2	O_2	CO	CH_4	H_2	N_2	Lb. Air per Lb. Gasoline	Per cent Completeness of Combustion
Results of tests at 10 mi. per hr. up 3 per cent grade												
3/4	1/2	988	0.3627	2.75	11.6	0.6	3.5	0.5	1.1	82.7	14.4	84
1	1/2	967	0.3492	2.87	11.4	0.6	3.7	0.4	1.5	82.4	14.4	83
1	1	985	0.3727	2.68	10.4	0.3	5.2	1.0	1.8	81.3	13.3	75
1	1 1/2	978	0.4071	2.46	9.9	0.3	6.6	0.7	3.2	79.3	12.5	72
1 1/8	2	978	0.4515	2.21	8.4	0.5	8.8	0.6	4.1	77.6	11.9	66
1 1/4	2 1/2	964	0.5011	2.00	7.8	0.5	9.5	0.8	5.1	76.3	11.5	62
1 1/4	3 1/2	848	0.6187	1.62	6.7	0.3	12.1	1.0	6.8	73.1	10.0	55
Results of tests at 6 mi. per hr. up 3 per cent grade												
3/4	1/2	566	0.4258	2.35	8.8	0.9	8.1	0.7	4.6	76.9	11.9	66
1	1/2	501	0.4467	2.24	8.0	0.9	9.5	1.0	5.0	75.6	11.1	62
1	1	516	0.4541	2.20	8.1	0.9	8.4	1.1	5.1	76.4	11.8	60
1	1 1/2	539	0.4726	2.11	Analysis indicated air leak in sample							
1 1/8	2	524	0.5379	1.86	7.8	0.7	9.4	1.9	5.3	74.9	10.7	56
1 1/4	2 1/2	539	0.6163	1.62	7.1	1.1	10.0	1.5	6.0	74.3	10.9	55
1 1/4	3 1/2	(1)	0.7516	1.35	5.8	2.0	11.1	2.8	5.6	72.7	10.0	47

[1] Mixture too rich for motor to develop normal power. Necessary to use lower gear for part of this test. The carburetor given this setting by service station carburetor adjustor as being correct for this unit.

REMARKS

The oil was carried high in crank case on all tests as it was considered light for this motor. This condition caused the exhaust to be smoky at times.

Gasoline Statistics

The nation's gasoline reserve is continuing its record-breaking climb, according to figures compiled by the United States Bureau of Mines, which show that on May 1 the total stocks on hand amounted to 892,267,766 gal., an increase of 38,000,000 gal. over the previous high record mark of April 1. While production records are being broken, the figures for the consumption of gasoline are also on an upward spurt. Thus, while domestic production for April 1922 registered an increase of 10.96 per cent over the production in April 1921, domestic consumption of this product in April 1922 shows an increase of 11.57 per cent over the consumption figures for April 1921. While the figures for domestic production plus imports of gasoline for April 1922 registered an increase of 13.43 per cent over similar figures for April 1921, the figures for domestic consumption plus exports and shipments for April of this year show an increase of 13.61 per cent over similar figures for the corresponding period last year.

The production of gasoline during April, which amounted to 472,920,182 gal., showed practically no increase over March. Total consumption figures, including exports and shipments to insular possessions, however, show an increase of 12,000,000 gal. Exports for April amounted to 58,007,495 gal.; shipments to insular possessions, 1,894,426 gal.; imports, 10,581,720 gal.; domestic consumption, 385,563,870 gal.

A daily average of 1,357,000 bbl. of oil was run through the stills of the 303 refineries reported to the Bureau of Mines as operating during the month of April. These figures show a decrease of 30,000 bbl. in the daily average run, and also three less operative plants than the report of the previous month. The April reports show operative plants to be running 77 per cent of their daily indicated capacity.

The seasonal decline in the gasoline stock curve, occurring generally during April or May, has not yet started, as is evidenced by the sharp increase in reserves.

Both production and stocks of kerosene showed an increase during the month of April. Stocks of this material on hand in May amounted to 325,836,126 gal. Production of kerosene in April amounted to 188,809,385 gal. Exports and shipments during the month consisted of 90,000,000 gal., this being the largest amount since December 1920.

Production of gas and fuel oil decreased 58,000,000 gal. during April, and stocks increased 32,000,000 gal., indicating a substantial decrease in the consumption of this product. The month's output of gas and fuel oil amounted to 791,642,710 gal., and stocks on hand May 1 amounted to 1,282,800,569 gal.

Production of lubricating oil in April amounted to 72,945,168 gal., the daily average production increasing 64,000 gal. during the month. Stocks of this product remained practically stationary, amounting on May 1 to 237,229,814 gal.

Prevention of Corrosion of Metals by Water in a Closed System[1]

By Perry West

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Metals rust to an appreciable degree only when they are in contact with both water and free oxygen. In all cases where water is confined in a closed system the free dissolved oxygen in the water is either the principal cause or the principal contributory element causing corrosion. The removal of this oxygen will in most cases practically stop corrosion, and in other cases materially reduce corrosion caused by other agencies.

Free carbonic acid gas promotes corrosion in the presence of free oxygen, but is practically inactive in its absence except at extremely high temperatures. Other free acids, such as nitric, hydrochloric or sulfuric, will cause corrosion if in proper concentration, but in their usual diluted state require the presence of free oxygen in the water to make their corrosive action very effective.

Carbonates of calcium and magnesium and other temporary alkaline salts may retard corrosion by depositing a protective coating on the metal and by acting as negative chlorides. At very high temperatures these carbonates may give off carbonic acid or caustic solutions, thereby promoting corrosion, especially in the presence of free oxygen.

Some chlorides, especially magnesium chloride, hydrolyze to form free acids, which are highly corrosive in the presence of free oxygen, but are not very corrosive otherwise, unless allowed to collect in strong concentrations. Carbonates and chlorides are both scale-forming and therefore provide some protection against their own corrosive action. This does not prevent pitting, which is the real measure of corrosion.

Sulfates and nitrates are more scale-forming than they are corrosive, but fail to act in either way except at high pressure boiler temperatures. At extremely high temperatures they may be dissociated and act as do chlorides at lower temperatures.

Increase in temperature increases corrosion. It is about ten times as rapid at 180° F. as it is at 50°, and at 210° it is again about ten times as rapid as at 180°.

Commercial processes for the elimination of dissolved oxygen depend on one of two methods. In the deoxidizing method the hot water is allowed to pass into a deactivating tank where it is brought into contact with thin sheets of specially prepared metal. The water exerts its corrosive activity on the comparatively cheap and easily replaced metal rather than on the piping system. The deaerating process removes the free dissolved gases from the water by heating, by vacuum, or by a combination of both while the water is sprayed over baffles in a deactivator. The latter process removes, of course, nitrogen, carbon dioxide, etc., as well as oxygen.

Gas-free water is not only noncorrosive, but also prevents scoring of engines, turbines, etc., by eliminating the dirt of corrosion. It also increases condenser efficiency from 20 to 25 per cent by eliminating the air blanket around the tubes, without requiring any more energy to remove the air before it enters the boilers.

The prevention of corrosion by the removal of free oxygen applies to brass as well as to iron and steel.

SCIENTIFICALLY, corrosion may be understood to mean the destruction of metals by some chemical or electrochemical action. Even in this field we have a great variety of actions: corrosion of metals in contact with atmosphere, corrosion of metals in contact with water, a combination of these, *i. e.*, of a metal in contact with water and air, and the various forms of corrosion caused by the action of the different acids, alkalies, and salts.

This article will describe one phase of these corrosive actions, namely, the simple corrosion which is usually caused by a natural uncontaminated water confined in a closed system.

Some striking examples of this kind of corrosion are to be found in the water piping, boilers, heaters, and tanks of buildings; in the feed systems, boilers, economizers, heaters, and pumps of power plants; in the various water handling systems of industrial works, and in the water handling systems and power plants aboard ship.

This is the simple oxidizing or rusting process. It has always been such a natural occurrence for iron in contact with water to rust that until quite recently it was taken as a matter of course that water always had and always would corrode this and certain other metals.

In just the same way there were many phenomena connected with corrosion which could not be explained by the simple assumption that the oxygen in the air or water alone oxidized or caused metals to rust. For instance, it was discovered that metals which corroded very easily in a damp atmosphere, corroded very little or not at all in an absolutely dry atmosphere; and also that metals which were ordinarily corroded by water failed to be acted upon under certain conditions. The piping systems of closed hot water heating plants, where the same water is circulated over and over, or the piping of sprinkler systems, where the same water is allowed to stand in the pipes, were discovered to undergo very little, if any, corroding action.

Starting with these and other known facts which seemed to indicate that it was not a matter of course for metals to be corroded either in air or in water, Mr. F. N. Speller, Metallurgical Engineer, of Pittsburgh, and Dr. William H. Walker, Professor of Industrial Chemistry at the Massachusetts Institute of Technology, started out a little over ten years ago to find out just what were the causes of the corroding action of water upon metals, and to devise some remedy for the cure of this enormously destructive action.

Up to that time most of the examples of corrosion already referred to were assumed to be perfectly natural hazards which were simply endured without any effective cure. Included in these were the corroding, pitting, and bursting of the hot water piping systems of buildings, with the resulting red and dirty water discoloration, and the costly repairing of pipes buried in walls, floors, etc., together with the continual annoyance, inconvenience, and repairs to building construction and decorations caused by leaky pipes. Other examples were the rusting away of the cold water piping of buildings, the corroding of the water pipes in power plants, industrial works, aboard ship, etc., and the corroding of boilers, economizers, engines, and turbines.

Theory of Corrosion

At the present time, the entire theory of this kind of corrosion has been very accurately worked out and very effective remedies have been developed. In the working out of these theories it has been conclusively shown that the rusting of metals does not take place to any appreciable degree unless the metal be in contact with both water and free oxygen, as the action at ordinary temperatures is practically nil where the metal is in contact with oxygen alone, or oxygen-free water alone. In other words, all three elements, namely, metal, water, and free oxygen, must be brought into contact. Once this fundamental fact is fully understood the whole subject of corrosion, of the character to which we are referring, becomes quite clear.

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[1] Presented at the 7th National Exposition of Chemical Industries, New York, N. Y., September 11 to 17, 1921.

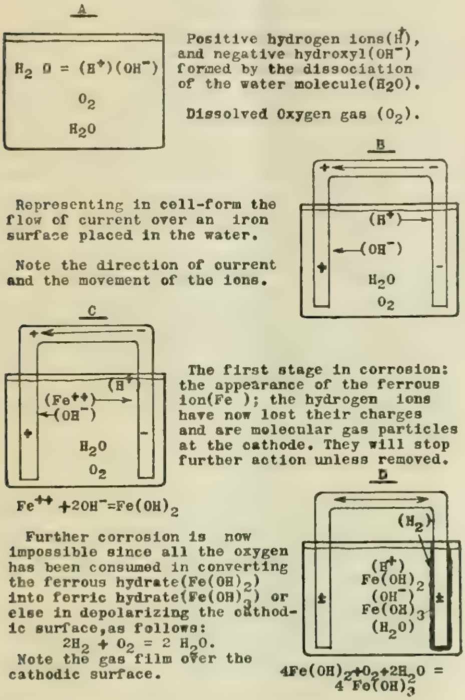
A
$H_2O = (H^+)(OH^-)$
O_2
H_2O
Positive hydrogen ions(H^+), and negative hydroxyl(OH^-) formed by the dissociation of the water molecule(H_2O).
Dissolved Oxygen gas (O_2).
B
Representing in cell-form the flow of current over an iron surface placed in the water.
Note the direction of current and the movement of the ions.
(H^+)
(OH^-)
H_2O
O_2
C
(H^+)
(Fe^{++})
(OH^-)
H_2O
O_2
The first stage in corrosion: the appearance of the ferrous ion(Fe); the hydrogen ions have now lost their charges and are molecular gas particles at the cathode. They will stop further action unless removed.
$Fe^{++} + 2OH^- = Fe(OH)_2$
D
(H_2)
(H^+)
$Fe(OH)_2$
(OH^-)
$Fe(OH)_3$
(H_2O)
Further corrosion is now impossible since all the oxygen has been consumed in converting the ferrous hydrate($Fe(OH)_2$) into ferric hydrate($Fe(OH)_3$) or else in depolarizing the cathodic surface, as follows:
$2H_2 + O_2 = 2H_2O$.
Note the gas film over the cathodic surface.
$4Fe(OH)_2 + O_2 + 2H_2O = 4Fe(OH)_3$

Fig. 1—Electrochemical Mechanism of Corrosion

Briefly stated, this theory of corrosion is: that the iron or other metal in contact with the water first dissolves, according to the solution pressure of the metal. The next step is that the dissolved metal hydrolyzes by combining with the hydroxyl radical in water and sets hydrogen free. This hydrogen tends to plate out on the surface of the iron as a result of very weak electrolytic currents set up between different parts of the metal, which act as battery plates, with the water as an electrolyte. The accumulation of small hydrogen bubbles on the surface of the iron tends to polarize these circuits and, unless disposed of, will very quickly create an equilibrium causing the above action to cease. In practice, however, there is always dissolved in natural waters enough free oxygen to combine with this hydrogen and prevent this polarization, thus allowing the action to continue as long as raw water is added to the system. This results in the formation of metallous hydroxide, which is the first stage of corrosion. The process would not proceed beyond this stage were it not for the further action of other portions of the free dissolved oxygen in the water. This oxygen continues to act, however, first to oxidize the metallous hydroxide to the metallic hydroxide, then to the metallous oxide which forms the metallic oxide, or in the case of iron or steel, ordinary red rust. The various stages of this process are shown diagrammatically in Fig. 1.

Effect of Acids, Alkalies, or Salts

In the foregoing, the corrosive action of water has been discussed without reference to the influence of any free acids, alkalies, or salts which it might contain. Inasmuch as most natural waters carry dissolved carbonic acid and some alkalies and salts, the natural question is—what bearing do these have upon corrosion?

CARBONIC ACID—Most natural waters contain a small percentage of free dissolved carbonic acid gas, which may be added to by the decomposition of carbonates and organic matter at high temperatures in heaters, boilers, etc. Carbonic acid gives the water a slight acid tendency which makes of it a better electrolyte and speeds up the above process, but inasmuch as this acid is not strong enough to form a salt of the metal or to dispel the hydrogen gas from the water, it will not force the action beyond the polarization stages unless free oxygen be present.

Carbonic acid will, therefore, speed up the rusting process only in case free oxygen is present, but will not cause appreciable corrosion in its absence.

STRONGER ACIDS—Stronger acids, such as sulfuric or hydrochloric, will of course attack the metal and cause corrosive action entirely apart from the actions discussed, provided they occur in proper concentration, but even these actions are very materially increased by the presence of free oxygen to keep the metallic surface more or less free of hydrogen. In such weak concentrations as are ordinarily found they are inactive without free oxygen.

CARBONATES—The general effect of the carbonates and some other temporary hardening alkaline salts is to retard corrosion. This is brought about by the protective coating deposited on the metal—especially if the water is heated—and by the alkaline reaction of these substances in the water. So marked is the influence of these temporary hardening salts upon corrosion that some of the harder waters, especially in limestone districts, are practically noncorrosive, except at very high temperatures. Some exceptions may be found to the rule in the case of sodium and some other carbonates which form caustics and acetates at high boiler temperatures, setting free oxygen, which in conjunction with each other increase, rather than retard, corrosion.

CHLORIDES—Some of the chlorides, especially magnesium chloride, will hydrolyze and partly dissociate into the hydroxide and hydrochloric acid, which combines with the metal of the pipes, etc., to form a metallic chloride, setting free hydrogen. The amount of hydrochloric acid thus set free in ordinary cases is very small, and, if allowed to act but once and then come to equilibrium, would cause comparatively little corrosive trouble.

If free oxygen be present in the water, however, which is usually the case unless particular pains have been taken to remove it, this free oxygen combines with the hydrogen set free, forming water and depolarizing the electrolytic circuit, thus allowing the process of corrosion to proceed. In the meantime the new metallic chlorides formed may re-hydrolyze, forming the metallic hydroxide and setting the hydrochloric acid free again. The process will then begin all over again and continue as an indefinite cyclic process, so long as there is enough free oxygen present to keep the electrolytic circuit depolarized. As new water is added additional hydrochloric acid is set free and if allowed to concentrate, as in boilers, is

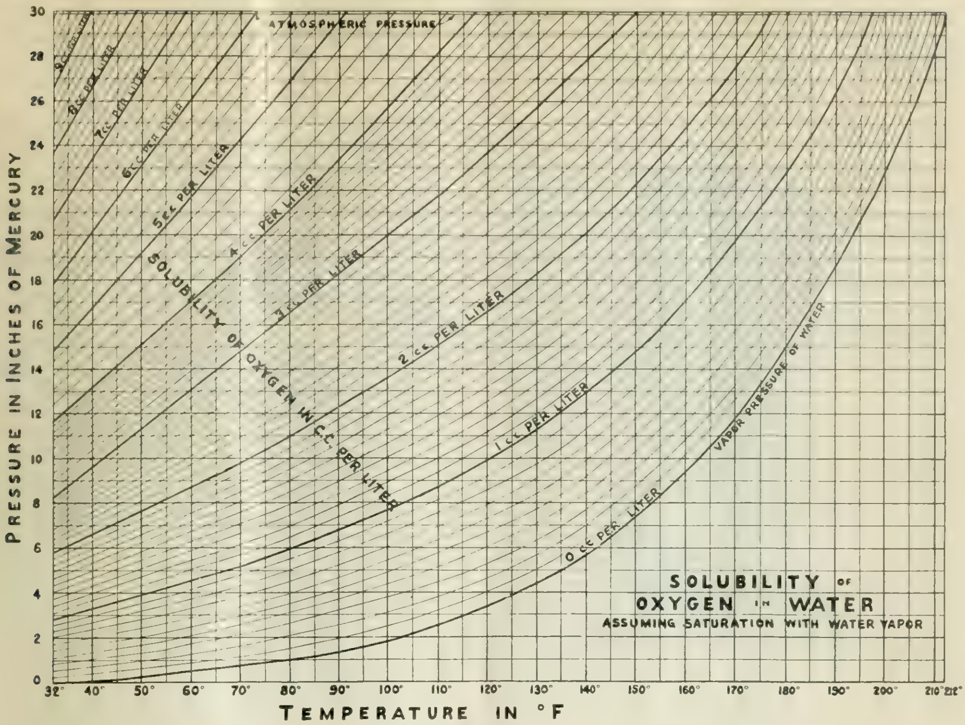

Fig. 2

one of the most dangerous corrosive agents met with in practice.

In the case of sea water, which is sometimes heated for bath purposes, this action is very marked and can be retarded only by neutralizing the acid or by the removal of the free oxygen from the water.

SULFATES AND NITRATES—In the case of power plants where high enough temperatures are carried in the boilers, economizers, etc., the sulfates and nitrates of calcium and magnesium may be broken up so as to act very much the same as the chlorides in the lower temperature systems. Sulfates and nitrates are not materially affected by the temperatures of ordinary domestic hot water, and have no particular bearing upon incrustation or corrosion in these systems.

It will be seen that soft waters and such hard waters as contain small quantities of bicarbonates are not scale-forming in ordinary domestic hot water systems and do not, therefore, tend to protect against corrosion in this way.

The foregoing gives a fair idea of the relationship between the chemical properties of the water and the subjects of incrustation and corrosion, from which it may be seen that a good chemical analysis of the water is a very helpful factor in designing apparatus for protection against corrosion.

Effect of Temperature

This corrosive activity, being an electrochemical action involving hydrolyzing and ionizing, naturally takes place much faster at high than at low temperatures. The corrosive activity in domestic hot water systems is, therefore, from five to ten times as rapid as in cold water systems, other conditions being equal. In the case of sea water the magnesium chloride augments the action so as to make corrosion with cold salt water almost as serious as with hot fresh water. In power plants the action may be many times as fast, depending upon temperatures. At 150° it may take as much as one hour to complete the corrosive action, while at a temperature of 212° one minute is sufficient.

Amount of Free Oxygen Present

Ordinary potable waters, with the exception of some deep well, or other ground waters, contain on an average about 5 per cent of dissolved air. Of this about 20 per cent is oxygen, which means about 1 per cent of oxygen by volume at ordinary temperatures and atmospheric pressure. The solubility of oxygen in water at various temperatures and pressures is shown in Fig. 2.

Much higher saturations may be reached under higher pressures such as are generally found with air pressure tank systems. Every pound of this oxygen may be responsible for at least 3 lbs. of corrosion, which means that for every thousand gallons of water about 0.25 lb. of iron or steel may be eaten away by this corrosion. Since the useful life of ordinary iron or steel pipe is practically ended by pitting when 20 per cent of its weight is corroded away, the rate of destruction in a hot water service system may run as high as 1.25 lbs. per 1000 gal. of water. This would mean the loss of about 1000 lbs. per year for an ordinary-sized building, which would represent a replacement cost of about $2000. It is estimated that the annual loss occurring in this way in domestic hot water service systems alone throughout the United States amounts to $50,000,000.

In domestic hot water systems a reduction to 1 cc. of free oxygen per liter of water may substantially stop corrosion, while with high temperatures in power plants it must be reduced to 0.2 cc. per liter.

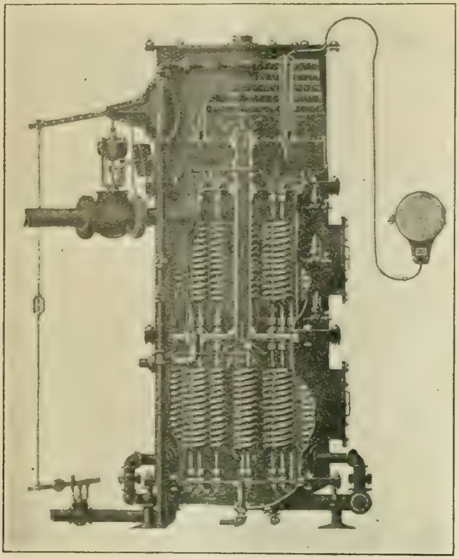

Fig. 3—Section through Deaerating Deactivator

Elimination of Dissolved Oxygen

As has been suggested, the way to prevent this corrosion is to eliminate the free oxygen. Some of the latest developments in commercial apparatus for eliminating dissolved oxygen will now be described.

Basically there are two methods, which may be designated as the deoxidizing method and the deaerating method. The deoxidizing process is carried on by allowing the hot water to pass from the heater into a tank or deactivator where it is brought into contact with thin sheets of perforated metal especially prepared, and arranged to allow the water to exert its corrosive activity upon this comparatively cheap and easily replaceable metal instead of the more expensive and less easily replaceable materials of the piping system. If the water is to be used for domestic or certain industrial purposes, it is then passed through a hot water filter to free it from the objectional discoloration caused by the products of corrosion in the deactivator, and is ready to use in the system without danger of any further corrosion or discoloration.

The deaerating process is carried on by removing the free dissolved gases from the water by heating, by vacuum, or by a combination of the two while the water is in a highly divided state brought about by spraying or cataracting over baffles in a deactivator. This process, as will be easily understood, removes not only the oxygen, but the other free dissolved gases, such as carbon dioxide, nitrogen, etc.

The removal of all gases eliminates airbinding and splashing difficulties, besides stopping corrosion.

Water treated by either process is sometimes termed deactivated water, meaning that it is minus its corroding activity.

The removal of oxygen by the deoxidizing process and the removal of the gases by the deaerating process amount to from 90 to 99 per cent of the quantities contained in the raw water in some of the commercial apparatus now on the market.

Numerous experiments have shown that the rate of corrosion is practically in proportion to the percentage of free oxygen present, so that a removal of 90 per cent means an increase of tenfold in the life of pipes and other apparatus protected.

The passage of deactivated water through an old corroded system not only prevents further corrosion, but will gradually dissolve and wash out the existing accumulations and keep the system clear and free from corrosion.

It is also interesting to know something about the cost of this apparatus and about the return it may be expected to show.

Ordinarily speaking, the cost of this apparatus will run from 5 to 10 per cent of the replacement cost of the materials protected. This means that the carrying and depreciation charges might amount to from 0.5 to 1 per cent of the replacement cost. Figuring on an average life of 10 yrs. for piping and apparatus without protection, it would mean that for a total cost of from 5 to 10 per cent of the cost of replacement the entire system may be protected and such replacement costs postponed practically indefinitely.

Another way of measuring the cost is on the basis of amortizing the cost of the apparatus over a period of 10 yrs. The sinking fund cost, together with the carrying charges, would amount to from 0.75 to 1.5 per cent per yr., and at the end of 10 yrs. the entire first cost and carrying charges would be wiped out, thus giving a fully paid-up insurance for the remainder of the life of the building.

Deaerating Deactivator

The apparatus shown diagrammatically in Figs. 3 and 4 consists of:

Type F deaerating deactivator
Water line governor X, controlling inlet valve W
Recording thermometer Y
Thermostat T, controlling steam valve S

The deactivator is constructed in three sections, A, B, and C, bolted together to form one unit. A is an exchanger, B is a booster heater, using low pressure steam, and C is a deaerator. The shells are $^5/_{16}$-in. open hearth steel, sections A and C being coated inside with the finest grade of porcelain enamel. The coils, pipes, pans, stay-rods and diaphragms are of cold-rolled copper or Tobin bronze, making for stability and long life; in fact, all working parts exposed to water contact are practically corrosion-proof.

The water which would normally pass directly down pipe D from the roof tank to the heater is by-passed through the deactivator around valve Z. While passing through coils G the water is heated up by exchange of heat from the hot water which is leaving the deactivator. The incoming water passes on through coils H, in which it is raised to 207°, the temperature being regulated by the thermostat T and the steam valve S. At this temperature the water readily gives up its dissolved gases as it falls over the cascade plates K. The deaerated, noncorrosive water leaves the machine via the exchanger section, in which it gives up a large part of its heat to the incoming cold water. The temperature of the water passing to the heater is approximately 120°.

Deoxidizing Deactivators

Two types of deoxidizing deactivators are shown in Figs. 5 and 6. In both of these types the raw heated water is passed through a deactivator filled with specially prepared, highly corrosive deactivating material. The design of the system is such that the water remains in contact with the metal long enough to expend substantially all of its corrosive activity upon the cheap, easily replaceable metal instead of upon the more expensive and less accessible metal of the piping and apparatus.

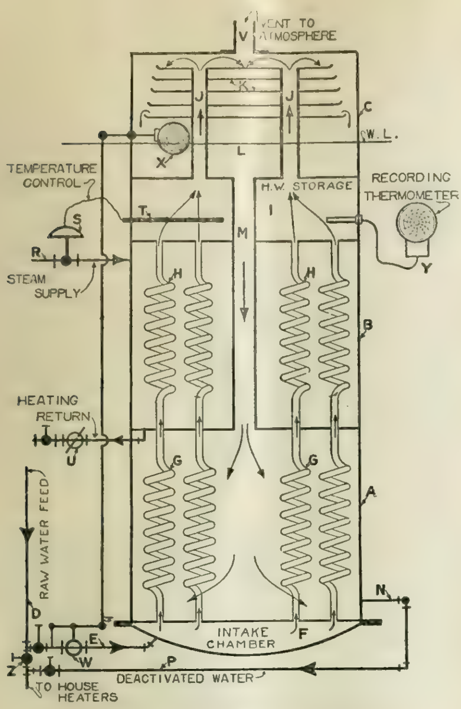

Fig. 4—Principle of Deaerating Deactivator

The type shown in Fig. 5 is the simplest possible arrangement of this apparatus. It is designed especially for use in large residences and small apartment houses. Any form of heater, coal, gas, garbage burner, or steam may be used. The cold water entering the heater is first passed through a coagulite tank where the water dissolves a minute quantity of coagulite which causes the colloidal rust to settle in the deactivating tank, thereby insuring a supply of clean, noncorrosive hot water.

For use in large apartment houses, or hotels, where sudden demands on the hot water supply service may be expected, a special hot water filter is added to the above equipment. The arrangement is as shown in Fig. 6. In an apparatus of this type, absolutely clear hot water is obtainable at all loads.

A small auxiliary heater is used to reheat the water returned by the circulation line as this returned water does not have to be deactivated again. Automatic temperature control, gages, and recording thermometer are usually supplied to control the operation of the apparatus and to provide a record.

Fig. 7 shows another type of deaerating deactivator intended for use where large volumes of water are to be treated under varying temperatures, usually from 100° to 200° F., for the removal of the free dissolved gases from the water so as to render it inactive toward the corrosion of iron and steel. This type of apparatus is especially applicable to the treatment of feed water for steam boilers, where the normal operating temperature of the water to be treated is not high enough to allow it to be treated economically in a simple "B" type deoxidizing apparatus. This is a condition usually met with in steam power plants where the available exhaust is only sufficient to raise the temperature of the feed water to a degree within this range and when there is quite a variation between high and low points and it is not desirable to reheat to a higher and more steady temperature with live steam on account of the extra cost and maintenance of auxiliary heaters, the decrease in efficiency of economizers, and the withdrawal of the high pressure steam from the supply to the prime movers. The effectiveness of this type is due to the fact that the bulk of the gases is removed by the vacuum deaerating process and the residual gas by the deoxidizing process, thus allowing each process to operate through its most economical range.

This system is applicable for the prevention of corrosion in feed piping, pumps, boilers, economizers, etc., in all kinds of central and industrial power plants, and is especially efficacious in the prevention of the very rapid and destructive corrosion which is following the introduction of steel tube economizers and other such steel and wrought iron apparatus as is being installed to meet the requirements of higher steam pressures and temperatures.

It is also obvious that any reheating of the feed water to a temperature above that afforded by the normal available exhaust steam serves only to reduce the efficiency of an economizer, so that this type of deactivator has an advantage wherever economizers are used.

The principle of operation and construction of the apparatus is briefly as follows:

The arrangement shown in Fig. 7 is for use in connection with the deactivation of feed water where an open feed water heater is to be used. A closed feed water heater or other means of heating the water to be deactivated may be substituted for the open feed water heater with certain slight modifications.

In the arrangement shown, the feed water is brought to the open heater in the usual way and is generally controlled by a water line governor and regulating valve as indicated. Instead of the open heater being vented to the atmosphere in order to free it of the noncondensable vapors, it is vented through pipes 1, 2, and 3 into pipe 4, and thence into the de-

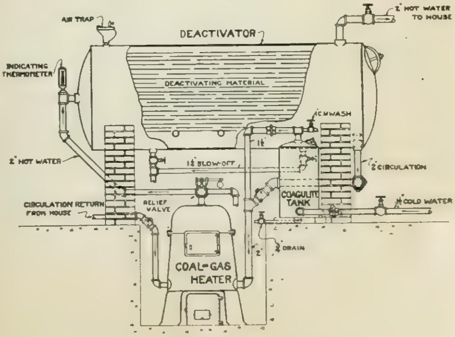

Fig. 5—Deoxidizing Deactivator, Type B-3

activator through perforated pipes 5 and 6, where all of the steam which passes over with these noncondensable vapors is condensed by mingling with the water entering the deactivator. This prevents the usual loss of steam to the atmosphere where the open heater is vented in the usual manner. Pipe 14 acts as an automatic emergency vent whenever the deactivator is shut down or the vacuum fails.

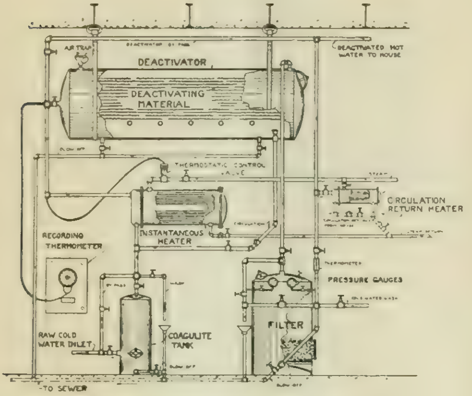

Fig. 6 Deoxidizing Deactivator, Type B-4

Located in vent line 4 is a low range vacuum governor for preventing anything more than a slight vacuum being carried on the feed water heater so as to prevent an excess of steam being carried over from the open heater to the deactivator. The water, leaving the feed water heater through pipe 7, passes either to the deactivator through pipe 8, or directly to the boiler feed pumps to pipes 9 and 10, as conditions may require.

A stop valve is located in pipe 9, for by-passing the water direct to the feed pump whenever the deactivator is out of operation.

The water in flowing to the deactivator passes through a differential vacuum governor chamber, which, together with the vacuum governor in the line leading to the deactivator, automatically maintains the vacuum in the deactivator at a point slightly below the boiling pressure corresponding to the temperature of the entering water.

From the inlet pipe the water passes to distributing pan 11, from which it flows to pans 12 and 13 over perforated pipes 5 and 6. As a result of the water being cataracted over a series of pans, and thus being broken up into small particles under a vacuum practically corresponding to the boiling point of the water, the major portion of the dissolved air and other noncondensable vapors are removed.

This process usually removes the free dissolved oxygen down to about from 0.75 to 0.5 cc. per liter, which is low enough substantially to prevent corrosion under certain conditions, but not low enough effectively to prevent serious corrosion in the feed piping, pumps, and steel tube economizers of the modern high pressure plant. In order to reduce this residual dissolved oxygen to 0.2 cc. per liter, which seems to be the practical condition under which serious corrosion is arrested, the water after leaving the deaerating process is passed through a thick body of deactivating material consisting of thin perforated sheets of specially prepared metal located in the lower section of the deactivator. The action of the residual oxygen on this metal is similar to what its action would otherwise be on the interior surfaces of the feed piping and economizers, causing the metal to corrode and fix the free dissolved corrosive gases. This metal, being of a cheap character and in an accessible place, is easily and cheaply replaced by way of the manholes or removable heads on the deactivator, thus transferring the corrosive destruction from the expensive and inaccessible materials of the plant to this inexpensive and accessible metal.

In certain cases where the volume of water handled or temperature conditions make it impractical to remove the residual oxygen by means of these metal plates, a chemical treatment is either substituted for the metal, or added to the deactivating system. It will be noted that the deactivator is provided with shut-off valves for use in case of emergency, and that the whole apparatus is simple and automatic in its operation.

In cases where head room will not permit, the heater may be placed nearer the level of the deactivator, but special arrangement must be made to allow the water to flow from the heater to the deactivator under vacuum. This arrangement is not advisable if it can be avoided. A head of from 3 to 6 ft. between the bottom of the deactivator and the feed pump suction is required.

The vacuum required for the operation of the system is usually produced by the regular vacuum pumps wherever condensers are used and requires no increase in the usual capacity of the dry vacuum pumps, since the air removed in the deactivator does not again have to be removed in the condensers. The required vacuum may of course be produced by a steam jet ejector or a separate vacuum pump wherever other vacuum producing means are not available, and requires very little power for operation.

It is of course understood that the removal of the free dissolved oxygen by this means or by other means is usually the most important factor in the prevention of corrosion in the feed piping, pumps, economizers, etc., and sometimes in the boilers themselves. Several other advantages, however, should not be overlooked. They will accrue wherever the dissolved oxygen and other noncondensable vapors are removed from the feed water. One of these is that the rust and sludge are caught in the deactivator and blown off in-

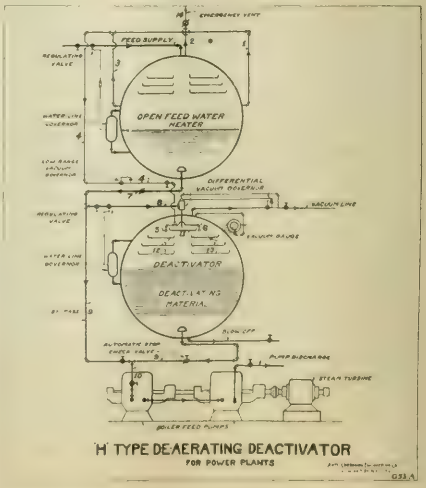

Fig. 7

stead of being allowed to pass to the boilers and form a very dangerous and uneconomical scale. Another is that the water is kept clean, which reduces foaming and prevents scoring of engine cylinders and the moving parts of turbines. Still another is that the efficiency of a surface condenser is increased from 20 to 25 per cent, on account of the absence of noncondensable vapors throughout the entire condenser instead of just around the dry air suction pipe under ordinary conditions.

The yearly saving effected by a deactivator of this type will show from 25 to 50 per cent on the cost of the installation, regardless of the other advantages enumerated.

Wood as a Chemical Engineering Material[1,2]

By Clark S. Robinson[3]

Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts

The value of wood as a material of construction in the chemical industries is very commonly underestimated. This arises from the fact that little information is available in the literature in regard to the use of wood for such purposes, and it is often true that on account of lack of information the plant operator makes use of unsuitable wood, or puts it to improper uses. It is the purpose of this article to give a fairly comprehensive outline of the various woods and their uses for chemical plant work.

Advantages

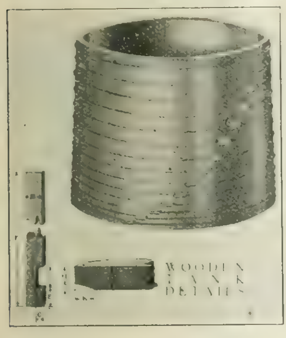

Fig. 1

Chemical apparatus made of wood is usually less expensive in its first cost than when made of metal. In many cases the difference in favor of wood is great. When used for water or other liquids which do not destroy the wood, the life of the wood is very long. Cypress tanks are known to have lasted for 130 yrs., while wooden water pipes have been in service underground for 100 yrs., such life being much in excess of that obtained from the ordinary steel of to-day. In many localities, the water contains material which quickly corrodes the best of steels while wood is quite unaffected. Wood does not require frequent painting to prevent corrosion as is the case with steel, and it can usually be repaired or remodeled by the local carpenter.

Wood is a poor conductor of heat, and wooden apparatus exposed to frost requires much less heat to keep the contents from freezing than is the case with metals. Conversely the contents of tanks and piping can be kept cold more easily when wood is used.

Wooden piping is not common in chemical plants, but it has many advantages, among which are the absence of corrosion due to electrolysis by stray electric currents, and its greater carrying capacity under given pressure drop. Its value may be indicated by the fact that one large chemical plant in this country has nearly one hundred miles of wooden pipe. Its cost is also less than that of iron or steel, considerably so in the larger sizes.

Disadvantages

Wood is not a suitable material for use in apparatus handling strong oxidizing agents, such as concentrated nitric or sulfuric acids. It is readily attacked by strongly alkaline solutions. It must be protected by a suitable protective coating from the action of certain chemicals, such as concentrated hydrochloric acid.

Wood is mechanically weaker than metals, and this limits the use to apparatus of comparatively moderate pressure, steel-banded wooden pipe having been used up to 130 lbs. pressure, and reinforced tanks up to 50 lbs. pressure.

Wooden tanks and piping swell when brought into contact with liquids, and shrink if allowed to dry out afterwards. This permits the joints of the apparatus to open up, and leaks develop. The apparatus must therefore be kept full of liquid and if this is not practicable, it should be filled with water to prevent drying out.

Kinds of Wood Available

The kinds of wood most commonly met with in this country are listed below in the approximate order of their popularity for chemical work in general.

1—Red Gulf or Louisiana cypress (*Taxodium distichum*)
2—Long leaf yellow or hard pine (*Pinus palustris*)
3—California redwood (*Sequoia sempervirens*)
4—White pine (*Pinus strobus*)
5—Douglas, Washington, or Oregon fir (*Pseudotsuga taxifolia*)
6—Hard maple (*Acer saccharum*)

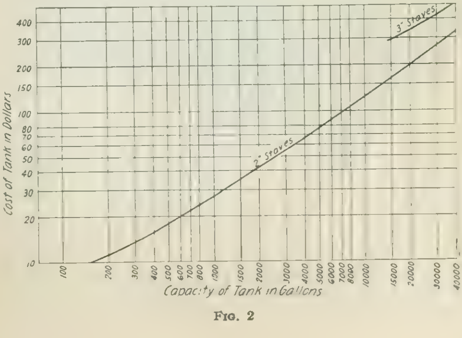

Fig. 2

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[1] Received April 4, 1922.

[2] Published as Contribution No. 17 from the Department of Chemical Engineering, M. I. T.

[3] Assistant Professor of Chemical Engineering.

7—Yellow poplar (*Populus deltoides*)
8—White oak (*Quercus alba*)
9—Tamarack (*Larix laricina*)
10—Spruce (*Picea rubra*)
11—Norway pine (*Pinus resinosa*)

TESTS ON EFFECT OF SOLUTIONS ON WOODS

A series of tests were performed by S. J. Hauser and Clarence Behrman for the Hauser-Stander Tank Company on the action of a number of common solutions on six woods: cypress, long leaf pine, Douglas fir, redwood, hard maple, and white oak. These tests included:

1—The contamination of the liquid by the extraction of coloring matter from the wood.
2—The absorption of liquid by the wood.
3—The swelling or shrinking of the wood.
4—The effect upon the strength and hardness of the wood.

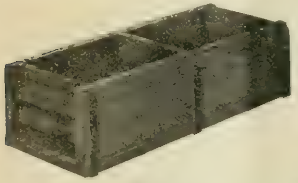
FIG. 3

COLOR—The color imparted to the liquid, while not important in many chemical operations, is frequently the determining factor in the use of wood for drinking water, for laundry purposes, and in the preparation of many food products.

Oak and redwood contain large amounts of coloring matter which is extracted freely by water both hot and cold, the redwood being a little the better with respect to the latter. Maple is better than oak or redwood, but is considerably worse than fir, pine, and cypress, the last of which has little effect on the water.

FIG. 4

Where wood is to be used for handling drinking water or for food products where a taste of the wood must be avoided, fir and pine should not be used. Cypress and maple are best in this respect.

The relative effect in the cold of various chemicals on the six kinds of woods with reference to color extracted is given in Table I. The effect is indicated by the numbers 1 to 4, 1 meaning little or no color and 4 strong color.

The *relative* effect of the above solutions when boiling hot is as a rule unchanged from when in the cold, though the colors are of course intensified in all cases.

ABSORPTION—The relative absorption of the same chemicals was studied. No relation between the concentration and the amount absorbed was apparent; so Table II gives the results for the average of several concentrations of each solution. Low absorption is represented by 1; large by 4.

TABLE I

SOLUTION	Cypress	Long Leaf Pine	Douglas Fir	Redwood	Hard Maple	White Oak
5% and 25% acetic acid	1	1	1	2	1	2
50% and 100% acetic acid	2	2	2	3	2	3
5% and 25% HCl	1	1	1	2	1	2
Concentrated HCl	4	4	4	4	4	4
10% H_2SO_4	1	1	1	3	1	3
25% H_2SO_4	2	2	1	3	2	3
5% HNO_3	4	4	4	4	4	4
1% NaOH	2	3	3	3	3	3
Concentrated NaOH	3	3	4	4	4	4
Saturated $Ca(OH)_2$	2	2	2	3	2	3
5% bleaching powder	1	2	2	2	2	2
Na_2S solution	4	4	4	4	4	4
5% Na_2CO_3	2	3	3	3	3	3
10% $NaHSO_3$	2	2	2	2	2	4
10% NaCl	2	1	1	2	2	2
10% $CaCl_2$	1	1	1	2	1	2
25% $CaCl_2$	1	1	1	2	2	2
Turpentine	2	2	2	2	2	2
Linseed oil	1	1	1	1	1	1

SWELLING AND SHRINKAGE—It was found that all the woods expanded in aqueous solutions and that a part of this expansion was lost upon subsequent drying. Some woods after treatment with nitric acid and the alkalies showed shrinkage after drying. Redwood showed the greatest swelling and oak the least.

FIG. 5

EFFECT ON PHYSICAL PROPERTIES—The effect of these solutions upon the softness, brittleness, and other physical properties of the woods was noted.

Acetic acid in any concentration has no effect on any of the woods.

TABLE II

SOLUTION	Cypress		Douglas Fir		Long Leaf Pine		Redwood		Hard Maple		White Oak	
	Hot	Cold	Hot	Cold	Hot	Cold	Hot	Cold	Hot	Cold	Hot	Cold
Water	3	2	4	3	3	3	4	3	4	4	4	4
HCl	4	2	4	3	3	2	4	3	4	4	4	3
H_2SO_4	4	2	4	2	3	3	4	3	4	4	4	3
HNO_3	2	2	3	3	3	2	3	3	4	4	4	4
Acetic acid	3	3	2	2	2	2	3	3	4	4	3	3
NaOH	4	4	4	4	3	4	4	4	4	4	4	4
Na_2CO_3	4	2	4	3	4	2	4	4	4	4	3	3
Na_2S	4	4	4	4	4	4	4	4	4	4	4	4
$Ca(OH)_2$	4	4	4	4	2	2	4	4	4	4	4	4
Bleaching powder	2	2	2	2	2	2	3	3	4	4	2	2
$NaHSO_3$	3	3	3	3	2	2	4	4	4	4	3	3
NaCl	3	1	4	2	3	1	4	3	4	3	3	2
$CaCl_2$	1	1	2	2	1	1	3	3	3	3	1	1
Turpentine	4	3	3	[illegible]	1	1	3	3	3	2	1	1
Linseed oil	3	2	3	2	1	1	4	3	2	2	1	1
Fatty acid	3	2	3	1	2	1	3	2	3	1	1	1

Dilute hydrochloric acid (5 per cent) makes redwood brittle, while 25 per cent acid has a similar effect on maple and oak; cypress, fir, and pine are unaffected. Concentrated acid destroys all woods.

Dilute sulfuric acid (5 per cent) has little effect on any of the woods, except redwood, which is made brittle. Cypress and pine are not seriously attacked by cold 25 per cent acid, but hot acid of this strength and concentrated acid destroy all woods.

Nitric acid has little action in the cold on cypress, fir, and pine in the 5 per cent concentration. The hot solution attacks all woods.

Maple, oak, and redwood are readily attacked by 1 per cent sodium hydroxide even in the cold, cypress and pine being unaffected up to 10 per cent boiling hot. Pine is not affected by cold 25 per cent sodium hydroxide solution.

Sodium sulfide up to 20 per cent concentration is destructive in the cold only to oak and redwood.

Hot sodium carbonate solution shrinks oak and softens redwood, and hot sodium chloride solution makes the latter brittle. The other woods are not affected.

These experiments indicate that, except for nitric acid and caustic soda, at least one of the six woods tested is suitable for each of the chemicals used, when in moderate concentrations. Cypress, fir, and pine are the woods least affected; maple and oak are for general use, of restricted value. There is considerable difference of opinion regarding redwood.

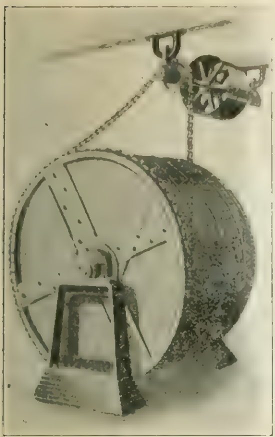

Fig. 6

Information Compiled by Forest Products Laboratory

A few years ago the Forest Products Laboratory compiled information from users of wood in chemical plants.[4] Experiences were very contradictory, but certain general conclusions could be drawn.

For pickling tanks cypress was the most popular, with white pine a close second. The other resinous pines were also used.

For hydrochloric acid, any variety of resinous wood, if impregnated with tar or other protective coating, was apparently suitable.

For acetic acid, any wood was satisfactory, with the possible exception of Douglas fir.

Cypress was preferred for saponifications and for most acid work, while long leaf pine was also very popular.

Filter press plates are usually made of paraffined maple, although other woods are sometimes used.

Tamarack is suitable for hydrofluosilicic acid up to 12 per cent and for dilute organic acids.

In general, the results of the compilation check very well the experimental results of Hauser and Bahlman.[5]

Solvents

Wooden apparatus for use with alcohol and other solvents should not be constructed of resinous woods, on account of the solvent action on the resins, but should be made up of either yellow poplar or white oak. The former imparts no color or taste to these liquids, but does not have the strength of the oak, which, however, gives up color readily to many of the liquids.

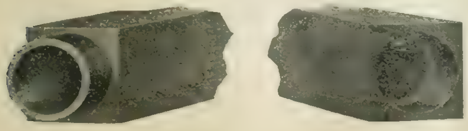

Fig. 7

Solutions which absorb water readily, such as certain hot concentrated solutions of hydroscopic salts, will, when brought into contact with wood, partly dehydrate it, causing it to shrink and to leak. Other materials such as hot tar have somewhat the same effect.

Hydrogen Peroxide

Maple has been found to withstand the action of 10 per cent solutions of hydrogen peroxide indefinitely.

Crystallizing Tanks

The use of wood for crystallizing tanks is unsafe only when the wood has absorbed large quantities of the saturated solutions. Under these conditions the tendency is to cause disintegration of the wood. If relatively nonporous wood be selected, wooden crystallizing tanks are very satisfactory and are long lived.

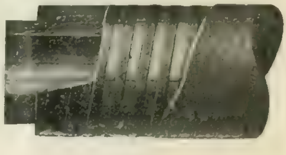

Fig. 8

Tanks

Round wooden tanks are constructed either straight or tapered. The construction of the bottom, the sections of which are held together by dowel pins, and of the stave, is shown in Fig. 1. The tanks are shipped ready to assemble according to directions furnished by the makers. The tanks should not be painted on the inside.

The tank hoops are usually made of steel, preferably round, although flat bands are sometimes used, with malleable iron lugs. In cases where the liquid handled will attack steel, monel metal, copper, brass, or other suitable metal should be used. Corrosion may be diminished by placing under the hoops wooden blocks on at least every alternate stave to hold the metal away from the sides of the tank.

The approximate cost at the present time of open top, round, wooden tanks for staves 2 in. and 3 in. thick is shown in Fig. 2.

The tanks should be so supported that all of the weight comes on the bottom and not on the staves, the ends of the latter clearing the floor by at least an inch.

Rectangular tanks are constructed as shown in Fig. 3.

These tanks are heavily rodded, the rods being made of resistant metals and completely buried in the wood where necessary to avoid corrosion. Long tanks must either have a partition as shown, or have external bracing. One company imbeds the rods in acid-resistant pitch.

Fig. 9

Tanks to withstand a vacuum are usually made with internal partitions, while for pressure external bracing with thick staves of strong wood such as oak is used. A typical pressure tank good for 40 lbs. pressure is shown in Fig. 4.

Agitators for wooden tanks can be constructed of either wood or metal. An all-wood stirrer is shown in Fig. 5.

Revolving drums of wood are used in tanneries. These must be specially braced at the ends to take care of the bearings. Such a drum is shown in Fig. 6.

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[4] *Chem. Met. Eng.*, **18** (1918), 528.

[5] For some further work on this subject see Abrams, "The Effect of Chemical Reagents on the Microstructure of Wood," This Journal, **13** (1921), 786.

PIPING

Modern piping for water is made of white pine. If the water carries in suspension abrasive solids, such as fine coal dust, hard maple is used and has been found to have about ten times the life of cast iron. For solutions of chemicals where white pine would be unsuitable, other more suitable woods could undoubtedly be used.

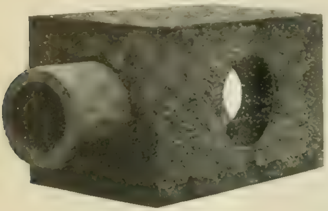

FIG. 10

Wood pipe is made either by boring out a solid log, or with stave construction. An example of the former is given in Fig. 7 which is a type suitable for laying directly on the floor of the plant, the flat sides preventing rolling. The wood stave pipe is made up as shown in Fig. 8. The staves are held together by a tightly wound steel band (copper is sometimes used for chemical work) and the whole pipe is then given a protective coating of asphaltic composition. The pipes are made with mortise (B) and tenon (A) joints, as shown in Fig. 9, and connection is made by driving the ends together, giving a joint of extreme tightness when swelled. Fittings for water are usually cast iron, but for chemical uses the wooden fittings are better. A typical tee is shown in Fig. 10.

TOWERS AND COLUMNS

Wooden towers and columns can be used advantageously for handling gases and vapors containing acid or other corrosive substances. The writer has seen an ordinary wooden silo filled with coke in very satisfactory use as a scrubber for furnace gases containing large amounts of sulfurous and sulfuric acids. Fig. 11 shows some acid towers of wood 60 ft. high by 6 ft. in diameter, at a paper mill.

FILTER PRESSES

Modern box filters are in common use in chemical plants and manufacturers of plate and frame filter presses supply presses of suitable woods for handling difficult liquors. Yellow pine plates resist alum solutions for from 6 to 10 mo.

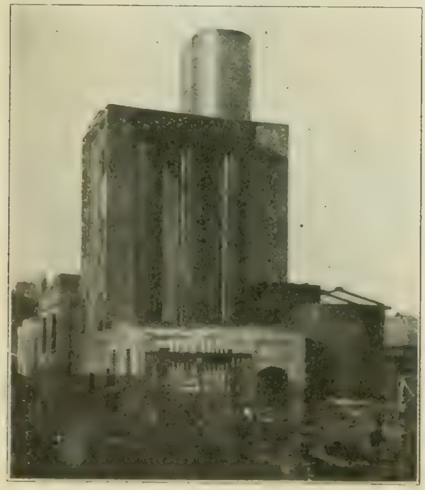

FIG. 11

PROTECTIVE COATINGS

Wooden apparatus is used successfully with corrosive liquids when protected with resistant materials. The most popular coating at the present time for acids is asphalt or pitch which has been thoroughly air-blown, applied in a layer at least 0.25 in. thick. Asphaltic paints and similar coatings are usually too thin to be of lasting value. Some concerns line wooden tanks with pure Para rubber with hard rubber fittings to withstand concentrated hydrochloric acid. Such tanks have lasted for 25 yrs. Lead lined wooden tanks are used for dilute sulfuric acid. As a general rule, however, it is better, except in difficult cases, as noted above, to leave the inside of the tank uncoated and unpainted.

ACKNOWLEDGMENT

The writer wishes to acknowledge the generosity of a number of the manufacturers of wooden equipment in furnishing data for the preparation of this article.

Apparatus of Transparent Bakelite for Measuring Hydrofluoric Acid[1]

By L. J. Curtman

DEPARTMENT OF CHEMISTRY, COLLEGE OF CITY OF NEW YORK, NEW YORK, N. Y.

GRADUATE

HAVING experimentally demonstrated that 48 per cent hydrofluoric acid was without appreciable action on transparent bakelite, the writer had a number of 10-cc. graduates made from this material. They have proved very serviceable in analytical work. Their shape is less flaring than the old style conical graduate but more so than the cylindrical graduate, in order to facilitate pouring hydrofluoric acid from the usual wax containers.

The advantages possessed by these graduates are:

1—They are not attacked by hydrofluoric acid.
2—They are transparent and hence permit the measurement of hydrofluoric acid.
3—They are less brittle than glass.
4—They are noninflammable.
5—They will not soften or become distorted.
6—They can be readily cleaned with hot water.

MEDICINE DROPPER

A medicine dropper made of transparent bakelite has been found vastly superior to the improvised lead tubes which have been used heretofore in carrying out one of the best qualitative tests for silica and silicates.[2] The transparent dropper enables one to see the quantity of hydrofluoric acid in the tube and thus to control the amount of acid to be transferred. It has the additional advantage over the lead or hard rubber tubes of being easily cleaned.

The graduate and dropper will soon be manufactured in quantity and will be offered for sale by dealers in chemical apparatus.

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[1] Received April 29, 1922.

[2] See A. A. Noyes, "Qualitative Analysis," 8th edition, 48.

Science Building at Tulane University

Construction has been begun on a new building at Tulane University which will accommodate the departments of botany, zoölogy, pharmacology, and physiologic chemistry. The building is to cost about $180,000, of which $125,000 have been subscribed by the General Education Board. The laboratory will be equipped at a cost of $30,000, and it is expected that the building will be completed in December.

Synthesis of Urea from Ammonia and Carbon Dioxide[1]

By Norman W. Krase and V. L. Gaddy

Fixed Nitrogen Research Laboratory, American University, Washington, D. C.

The following paper describes the development of a process for the synthesis of urea from ammonia and carbon dioxide. The process consists in the preparation of ammonium carbamate, autoclaving to cause partial conversion to urea, distillation of the resulting sludge to separate the urea from the unconverted ammonia and carbon dioxide, and condensation of the distillate with additional gas to form a new charge. A small-scale experimental plant for testing the process was built and operated.

A discussion of the conversion reaction from a theoretical standpoint is given.

Cost considerations lead to the conclusion that the cost of urea by this process would be largely dependent on the cost of ammonia. It seems possible that the process might have commercial significance for the production of urea for fertilizer purposes, and in any case the process is of interest for the production of urea for its present uses in the arts.

LIMITATIONS on the use to which urea has been put may be ascribed almost entirely to the difficulties and cost attendant upon its commercial production. In recent years the greater part of the urea manufactured in this country has been produced from crude calcium cyanamide. The present cost of urea obtained in this manner limits its use to high-grade products.

The chemical characteristics of urea make it adaptable in many arts; its suitability as a stabilizer in explosive mixtures, as a constituent of varnishes and an ingredient in the transparent celluloid used for photographic films, as a factor in organic syntheses and medicinal preparations is outstanding evidence of the usefulness of urea in technical processes. In recent years, other uses for urea have been discovered, the developments of which have been checked by cost considerations. Foremost among these latent possibilities is the use of urea for fertilizing purposes. Many references[2] could be cited showing the value of urea as a nitrogenous fertilizer. It is logical to infer that greater and more varied uses for urea await improvements in methods for its synthesis.

The materials required in the process herein described are ammonia and carbon dioxide. Sources of ammonia are by-product coke ovens and nitrogen fixation plants using either the cyanamide or Haber process. Carbon dioxide is a waste product of many industries and can readily be concentrated if necessary. It should be pointed out, however, that a plant for the synthesis of ammonia by the Haber-Bosch process, in which hydrogen is produced by the water-gas reaction, also supplies carbon dioxide in large amounts. The gas coming from the water used in scrubbing the nitrogen-hydrogen mixture contains 70 to 80 per cent carbon dioxide and seems entirely adaptable for use in the synthesis of urea by the process to be described. Carbon dioxide may also be obtained from limekiln gas, which contains 15 to 40 per cent carbon dioxide, depending on the type of kiln or retort. The carbon dioxide content of the gas may be increased by absorption in water at moderate pressures (25 atmospheres) exactly as carried out in the water scrubbers of a Haber plant.

Previous Work

Basaroff,[3] in 1870, found that "considerable" quantities of urea could be obtained by heating ammonium carbamate in sealed tubes at a temperature between 130° and 140° C. He also found that commercial ammonium carbonate is partly converted to urea by similar treatment, but no yields are given. Herroun,[4] in 1881, discovered that urea and ammonium cyanate are formed when a mixture of air with the vapors of benzene and ammonia solutions is passed over a heated platinum wire and subsequently cooled. These experiments were performed in simple laboratory apparatus and yielded only sufficient product to serve for analysis. Mixter,[5] in 1882, synthesized urea from ammonia and carbon dioxide by passing the mixed gases through a hot tube at atmospheric pressure. Urea was formed at the rate of 10 to 15 mg. per hr.; the quantity of ammonia used per hour is not stated, however. Bourgeois,[6] in 1897, carried out experiments very similar to those of Basaroff, and by alternate heating and cooling with release of pressure managed to obtain a 6 per cent conversion to urea. Finally, in 1911, the reaction was investigated quite thoroughly by Fichter and Becker.[7]

Theoretical Considerations

In August 1919, this Laboratory began an investigation of the synthesis of urea from ammonia and carbon dioxide. Preliminary experiments were performed with ammonium carbamate, which was made by passing ammonia gas and carbon dioxide into absolute alcohol according to the method of Mente.[8] The ammonium carbamate was sealed in heavy glass tubes and heated at different temperatures for several hours. After cooling, the contents of the tubes were removed and analyzed for urea. The yields of urea were extremely low. It was later realized that several important factors influencing this reaction were not at first fully appreciated. These factors are brought out by a consideration of the thermochemistry and thermodynamics involved and will be briefly discussed.

The formation of urea from ammonium carbamate is essentially expressed by the equation:

$$\underset{\text{Ammonium carbamate}}{(NH_3)_2CO_2} \rightleftharpoons \underset{\text{Urea}}{CO(NH_2)_2} + \underset{\text{Water}}{H_2O} - \text{heat}$$

The equilibrium for this reaction in dilute solutions has been determined by Lewis and Burrows[9] at 77°, 110°, and 132° C. Applying van't Hoff's equation, the data of Lewis and Burrows lead to the value −6400 cal. for the heat of reaction, while Matignon and Frejacques[10] give for the heat of the reaction the calculated value −6000 cal. and state that the experimental value is −7700 cal. The method of experimentally determining the heat of reaction is not stated. In any case, the data are sufficient to show that the reaction is endothermic and that improved yields of urea will be obtained as the temperature is raised.

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[1] Received March 8, 1922.

[2] *Mitt. deut. Landw. Ges.*, **31** (1916), 16, 90, *Jahrb. deut. Landw. Ges.*, **34** (1919), 305; *Wochschr. Brau.*, **36** (1919), 355.

[3] *J. prakt. Chem.*, [2] **1** (1870), 283.

[4] *J. Chem. Soc.*, **39** (1881), 471.

[5] *Am. Chem. J.*, **4** (1882–83), 35.

[6] *Bull. soc. chim.*, [3] **17** (1897), 474

[7] *Ber.*, **44** (1911), 3473.

[8] *Ann.*, **248** (1888), 235.

[9] *J. Am. Chem. Soc.*, **34** (1912), 1515

[10] *Bull. soc. chim.*, **31** (1922), 101.

Although the data of Lewis and Burrows for the equilibrium in this reaction are undoubtedly satisfactory for dilute solutions, nevertheless the extrapolation of their results to the concentrated "melts" or solutions obtained in actual practice can hardly be very reliable. A very rough calculation can be made, however, on the assumption that the fugacities of carbamate, urea, and water are proportional to the molal fractions of the three substances.

At 132° C., Lewis and Burrows obtained a solution which contained 0.967 g. of carbamate, 0.0331 g. urea, and 1.511 g. of water. Considering the mass law expression where f^1, f^2 and f^3 are the fugacities of carbamate, urea, and water, respectively, we obtain from the data of Lewis and Burrows,

$$K = 0.0385.$$

An analysis[11] was made of a solidified "melt" resulting from heating pure ammonium carbamate at 125° C. in a sealed tube. The total weight of the "melt" was 1.5464 g. Its urea content was 0.4089 g. Since water and urea are formed in equivalent quantities we may take the water content as equal to

$$\frac{18}{60} \times 0.4089 = 0.1227 \text{ g.}$$

Calculating the molal fractions and substituting in the mass law expression, we obtain

$$K = 0.134.$$

It will be noted that even though the temperature is lower than that at which Lewis worked, the equilibrium constant is considerably larger. This must be due to the incorrectness of our assumption that the fugacities of the substances involved are proportional to their molal fractions. In all probability the fugacity of the carbamate increases much more rapidly than its concentration because of the decreased hydrolysis in concentrated solutions. From the point of view of the manufacture of urea by this process it is very fortunate that higher yields can be obtained than would have been predicted from an extrapolation of the data of Lewis and Burrows.

In connection with any attempt to make theoretical calculations as to the yield to be expected it must be noted that the system is really one of great complexity. We have very little information concerning the hydrolysis of ammonium carbamate, and other secondary reactions may occur in the "melt," as will be noted from the following list:

$$\begin{aligned}
(NH_3)_2CO_2 + H_2O &= (NH_4)_2CO_3 \\
(NH_4)_2CO_3 &= NH_4HCO_3 + NH_3 \\
NH_4HCO_3 &= NH_3 + CO_2 + H_2O \\
(NH_4)_2CO_3 &= 2NH_3 + CO_2 + H_2O
\end{aligned}$$

FURTHER EXPERIMENTAL WORK

From the considerations just mentioned we can conclude that the commercial success of the process lies in the ability to utilize solid ammonium carbamate as the starting material and that the highest practicable temperature should be employed. The glass tube experiments were continued in order to determine the influence of other factors. This laboratory was soon able to establish conditions under which a conversion of approximately 40 per cent of the total ammonia to urea could be consistently obtained.

It is evident that since the equilibrium is established in the liquid phase and presumably only a negligible amount, if any, of urea is in the gaseous phase, the extent of conversion is dependent on the ratio of the volumes of liquid and gas phases. Accordingly, experiments were conducted in which the weight of ammonium carbamate in a given reaction volume was varied between wide limits. The density of packing, as measured by the grams of carbamate per cubic centimeter of the volume of the container, was found to be an important factor in determining the yield, as is shown in Fig. I.

Another factor whose influence it was desirable to determine is the per cent of water present in the original carbamate.

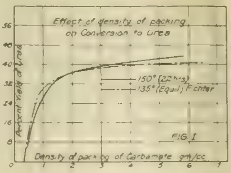
FIG I

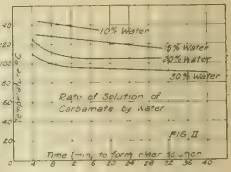
FIG II

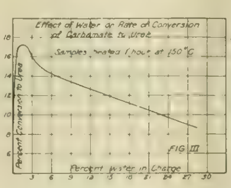
FIG III

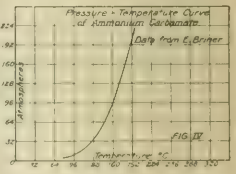
FIG IV

In order to obtain some qualitative information on this point, a number of mixtures of carbamate and water were subjected to different temperatures and the time interval necessary to form a clear solution noted. This time interval is a measure of the rate of heat conduction through the mixture, and while it is, of course, dependent on the dimensions of the container, it does give a qualitative measure of the rate of heat transference through the charge. Fig. II shows these results graphically. The effect of water on the rate of the reaction is, of course, intimately connected with this, and the results of experiments in which mixtures containing different percentages of water were heated for 1 hr. at 150° C. are graphically shown in Fig. III. The very rapid increase in the rate of the reaction with the addition of small percentages of water is noteworthy. It is believed that this effect is due primarily to the better heat conductivity of the material containing water. Additions of water greater than about 1.5 per cent apparently result in a partial reversal of the reaction.

The laboratory experiments just described yielded the information that solid ammonium carbamate is the best starting material for the urea conversion reaction and that the yield of urea is markedly dependent on the density of packing of the charge. Qualitative information regarding the effect of water on the rate of heat conductance through the charge and the effect of water on the rate of conversion was obtained. The further developments arising from the operation of a small-scale plant will now be described.

EXPERIMENTS WITH SMALL EXPERIMENTAL PLANT

PREPARATION OF AMMONIUM CARBAMATE—Previous workers in this field have used the method of Mente,[8] in which ammonia and carbon dioxide are passed into cold absolute alcohol, ammonium carbamate separating out. The use of absolute alcohol, of course, limits the use of this method to a laboratory scale. Another objection is that it is impossible to remove the last traces of alcohol from the precipitated carbamate. According to Fichter and Becker,[7] traces of alcohol exercise an inhibiting effect on the formation of urea, but the present writers have not been able to substantiate this. An analysis of their data indicates that more than one influencing factor was varied at one time, and the decreased yield may be in part accounted for by a decreased density of packing.

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[11] The authors are indebted to Messrs. E. J. Fox and L. Pinck of this Laboratory for analytical assistance in connection with this investigation.

Other known methods of preparing ammonium carbamate involve the use of nonaqueous liquids in which carbamate is not appreciably soluble, the condensation of gaseous mixtures on cold surfaces, or the use of liquid ammonia and gaseous carbon dioxide.

In view of the fact that this Laboratory was contemplating a series of investigations in which about 10 to 12 lbs. of ammonium carbamate would be used during a single conversion experiment, it was necessary to develop a method for conveniently preparing large quantities of this material. The use of liquid ammonia and gaseous carbon dioxide was thoroughly tested, with several gallons of liquid ammonia at a time. It was concluded that this method of preparation was wasteful of ammonia and too expensive to warrant further consideration. Another factor that largely determined the course of further experiments developed after some conversions had been carried out in the large autoclave. It was realized that the urea formed from ammonium carbamate would be mixed with water and unchanged ammonium carbamate, since an equilibrium had been definitely established at approximately 40 per cent conversion. The logical method of separation was to distil off the ammonia, carbon dioxide, and some of the water, and to recondense the vapors to form ammonium carbamate for a repetition of the conversion reaction. In fact, the whole success of the process of producing urea from ammonium carbamate seemed intimately linked with the development of a condenser to recover the unchanged ammonia for further use in the process. Data on which to base a reliable calculation as to the capacity and efficiency of a condenser were not available. An apparatus suitable for investigating this point was therefore constructed.

CONDENSATION OF MIXTURES OF AMMONIA, CARBON DIOXIDE, AND WATER—The vapor pressure temperature relations of ammonium carbamate at temperatures from 80° to 200° C. have been carefully measured by Briner,[12] whose results are shown graphically in Fig. IV. In order to extend this curve to lower temperatures, data have been collected from other sources, as indicated in Table 1.

TABLE 1—VAPOR PRESSURE OF AMMONIUM CARBAMATE

TEMPERATURE ° C.	VAPOR PRESSURE Cm. Hg	SOURCE OF DATA
0	1.24	M. and F.[1]
10	2.98	M. and F.
20	6.20	M. and F.
30	12.40	M. and F.
40	24.80	M. and F
50	47.00	M. and F.
55	60.00	M. and F.
60	77.00	M. and F.
77.2	227.00	B.[2]
81.0	240.68	M. and F.
98.5	640.00	B.
100	686.00	M. and F.

[1] Matignon and Frejacques, *Compt. rend.*, **170** (1920), 462.
[2] Briner, *J. chim. phys.*, **4** (1906), 266.

From these data it is possible to calculate by means of the Clausius-Clapeyron equation, the heat of condensation (or vaporization) of ammonium carbamate. Between the temperatures of 80° and 25° C. the heat of condensation as given by this equation is 12,380 cal. per mole (78 g.). The separation of the unchanged carbamate from the urea would probably be effected by distillation at a temperature not exceeding 80° C. because of the instability of urea at higher temperatures. The advantages of condensing carbamate at about 25° C. are obvious. The association of such large quantities of heat with the condensation (or vaporization) of this compound is evidently due to the fact that in addition to the latent heat we must include the heat of combination (or dissociation) of ammonia and carbon dioxide, since the vapor of ammonium carbamate is a mixture of these two separate gases.

In addition to the necessity of removing such large quantities of heat from the condensate it was known that solid ammonium carbamate is a very poor conductor of heat; consequently the writers were confronted with the problem of removing this heat through a layer of ammonium carbamate which, as previously mentioned, is a very poor conductor of heat. The methods in commercial use for the preparation of similar compounds, such as ammonium carbonate, employ very large surfaces on which the vapors slowly condense. The condensate is removed by breaking off the layers either by mechanically beating the large metal sheets that form the condensing surface or by other similar and equally cumbersome processes. These methods do not appear to be applicable to the present process, especially in the case of small installations where compactness of apparatus is essential. It appeared that a limited surface kept constantly cold, and from which the condensate could be continuously removed by some sort of scraping device, would be a better solution of the problem.

The condenser used in this work was designed to operate on this principle and consisted essentially of a cylindrical tube surrounded by a jacket in which the cooling medium was circulated and provided with a rotating, scraping blade fitting closely inside the cooled tube. The mixed gases, ammonia and carbon dioxide, together with the desired quantity of water vapor, were led into the upper end of this tube and condensed out on the cool walls from which the condensate was continuously removed by the revolving blade.

CONDENSATION EXPERIMENTS—In order to determine the efficiency, capacity, and operating characteristics of the condenser, an investigation of the condensation of measured quantities of ammonia, carbon dioxide, and water was undertaken. For this work the two gases, ammonia and carbon dioxide, were separately measured by means of calibrated orifice meters; the carbon dioxide was then passed through a saturator containing water at such a temperature that the desired quantity of water was carried along with the gas. The ammonia and humidified carbon dioxide were then led through a chamber and intimately mixed at such a temperature that no condensation occurred. From the mixing chamber the gases entered the condenser where the gas mixture came into contact with the cold condenser wall and deposited out in a layer that was continuously scraped off by a blade revolving at about 50 r. p. m. The condensate was allowed to fall into a hopper provided at the lower end of the tube.

A series of experiments were made with different rates of flow of gas into the condenser and different percentages of water in the gas. In each case the ratio of the volumes of ammonia to carbon dioxide was 2 : 1 as in ammonium carbamate. Results of these experiments are graphically shown in Fig. V. Examination of these curves reveals a characteristic relation between the rate of flow of the gases into the condenser and the efficiency of condensation. With a fixed percentage of water each curve shows a definite maximum efficiency which decreases when the rate of gas flow is raised or lowered. It is probable that this region of maximum efficiency is a function of the turbulence of the gases in the condenser and of the space velocity. It is also noteworthy that the efficiency is dependent on the water content up to a limiting value of about 1 per cent. The curves comprising Fig. VI show the effect of the rate of gas flow on the capacity, or hourly production, of the condenser. It is seen that with a fixed water percentage the capacity increases to a constant value which represents the maximum output of ammonium carbamate with a specified water content regardless of the amount of gas sent into the condenser. Sufficient data have been collected from these experiments to afford a basis for an approximate calculation of the efficiency and capacity of larger condensers of the same general type.

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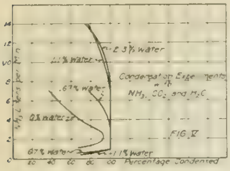
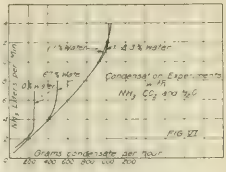
[12] *J. chim. phys.*, **4** (1906), 266.

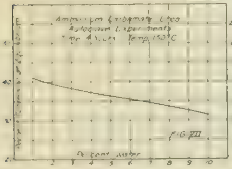


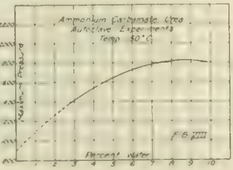


USE OF AMMONIUM CARBAMATE BRIQUETS—In all other processes of a similar nature, and in the several German patents on the process, it is apparently necessary to cool down the autoclave before each introduction of the charge. The volatility of ammonium carbamate and its high vapor pressure at elevated temperatures served to increase the difficulties. Finally, however, the idea of forming carbamate into a briquet of such a size as to enter the autoclave easily was adopted. Experiments on briquetting the charge showed that the material was well suited to the production of strong and easily handled briquets even when subjected to the small pressures available in the simple briquetting press that was assembled for these experiments. A test of loading the autoclave, previously heated to the working temperature, 150° C., with one of these briquets was then made. The entire practicability of this method of loading was demonstrated in an apparatus that was not entirely suitable for a fair test since the operation of closing the autoclave after the introduction of the charge was unnecessarily slow. With a properly designed rapid closing head, no difficulty should be experienced in introducing the charge without cooling the autoclave.

Experiments were then continued. The results of the glass tube experiments were substantiated, the yield of urea being consistently in the region of 40 per cent; that is, 40 per cent of the ammonia originally present in the charge of carbamate was converted to urea in the course of approximately 4 hrs. In one experiment a conversion of 41.1 per cent was obtained.

CONVERSION EXPERIMENTS—Examination of the vapor pressure curve in Fig. IV shows the high pressures that the autoclave in which the conversion reaction is carried out must withstand. Consequently, the autoclave used in these experiments was tested to a pressure of 2500 lbs. per sq. in. previous to its use. The working pressure was calculated to be between 1200 and 1800 lbs. per sq. in. It was known that ammonium carbamate under the conditions of the conversion attacks steel. The parts coming into contact with the charge were therefore protected by a thick layer of tin.





The main body of the autoclave was a section of extra heavy steel pipe 18 in. long and 4.75 in. inside diameter. The pipe was threaded at both ends to receive flanges, to which in turn were bolted the top and bottom flanges that closed the openings at each end. A steam jacket around the pipe and suitable means for measuring the pressure and temperature of the charge were provided. The capacity of the finished autoclave was 0.174 cu. ft. or 4.93 liters, and it was capable of containing 12 lbs. or 5500 g. of ammonium carbamate.

EFFECT OF WATER ON THE CONVERSION

The effect of water on the conversion reaction was first studied, since it was necessary to know the limits within which good yields could be obtained. Autoclave charges were prepared containing percentages of water ranging from 1 to 10. These charges were carried through the conversion reaction, and the yield was noted in each case. The results are shown graphically in Fig. VII. As was expected, the addition of water to the system

$$(NH_3)_2CO_2 \rightleftharpoons CO(NH_2)_2 + H_2O$$

resulted in a partial reversal of the reaction and a consequent decrease in the percentage of ammonia converted to urea. The figure shows that each per cent of water added lowered the conversion approximately 1 per cent. There is, therefore, considerable latitude permissible in the operation of the condenser, since variations of several per cent in the water content of the ammonium carbamate cause only a small loss in the conversion.

EFFECT OF TEMPERATURE ON THE CONVERSION

The temperature at which the conversion reaction is carried out was shown by the preliminary experiments to have a marked influence on the equilibrium. A study of this factor was next made. Two charges, each containing 7.5 per cent of water, were autoclaved; one was heated at approximately 150° C. for 4 hrs., the other at approximately 140° C. for the same period. The yields were 34 and 19.75 per cent, respectively. These very significant results indicate that the reaction is endothermic and is probably accompanied by an appreciable heat change. It is, therefore, very desirable to maintain as high a temperature as possible during the course of the conversion. The limitation on the extent to which the temperature may be increased is evident from the vapor pressure curve already referred to (Fig. IV) and involves mechanical considerations regarding the strength of the autoclave.

EFFECT OF WATER ON THE EQUILIBRIUM PRESSURE

The experiments to determine the effect of water on the equilibrium showed that the maximum pressure of the system was dependent on the original water content of the charge. This relation is shown in Fig. VIII. Matignon and Frejacques[13] while working with dry carbamate obtained a pressure of 55.09 atmospheres (810 lbs. per sq. in.) at 150° C. This is close to the value, approximately 900 lbs. per sq. in., obtained by an extrapolation of the curve in Fig. VIII to 0 per cent water. It may be noted that an increase in the percentage of water is accompanied by an increase in the total pressure of the charge. A possible explanation of this surprising fact is that a change in the gaseous equilibrium results, due to a change in composition of the liquid phase. As the conversion proceeds, water is formed and, if we may make the somewhat doubtful assumption that increased percentages of ammonia are being removed from the gas phase because of its greater solubility in water, we must expect an increased total pressure as the equilibrium adjusts itself by an increased partial pressure of carbon dioxide.

It will be noted that the pressures obtained are of the same magnitude as those used in the Haber process for the synthesis of ammonia. The problem of designing apparatus to operate at these pressures is, however, much simpler since we are dealing with a much lower temperature and with heavier gases, and consequently the question of the porosity of metals to gases does not enter. Moreover, it is necessary to maintain this high pressure only in one stage of the process and not in pipe connections where ordinarily great difficulties arise. Furthermore, it is necessary to use autoclaves of small diameter in order to cause rapid transfer of heat through the charge, and therefore the difficulties of holding the pressure are much reduced. Only mechanical considerations limit the height of the autoclave.

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[13] *Compt. rend.*, **171** (1920), 1003

Distillation of Autoclave Sludge

One step in the process still to be investigated was the distillation of the autoclave sludge, to separate the unconverted ammonium carbamate and condense it for further use in the process. For these experiments actual sludges, formed by the conversion of the carbamate charge, were discharged into the still.

The composition of the sludges was approximately the same for all distillation experiments; 40 per cent of the total ammonia was in the form of urea, and the remainder was combined with carbon dioxide in the proportion of two moles of ammonia to one of carbon dioxide. A quantity of water equivalent in moles to the quantity of urea was also present.

The sludge was released slowly from the autoclave into the still and cooled to about 57° to 59° C. In order to insure uniform composition in all parts of the sludge and to facilitate the escape of vapor, the still was equipped with a stirring device. Fig. IX shows the complete installation. The still was provided with a jacket and fitted up so that either cooling water or steam could be circulated.

The results of the conversion experiments indicated that about 40 per cent of the ammonia would be removed from each charge as urea. Assuming that the remaining 60 per cent could be recovered by distillation and condensation, it became necessary to make up this deficiency during the formation of the new autoclave charge. The most direct method was to introduce the "make-up" gases into the gas stream distilling from the sludge and thus utilize the same condenser for both purposes—recovery and "make-up" of the deficiency. This procedure was thoroughly tested.

DISTILLATION EXPERIMENTS—In the first experiments on the distillation of sludges the gases were allowed to pass over into the condenser as a result of their own vapor pressure. Additional or "make-up" ammonia and carbon dioxide were mixed with these vapors just before their entrance into the condenser. The course of the distillation could be followed from the results of analyses of the sludge residue taken from time to time during the distillation. The amount of "make-up" gas was determined by metering the ammonia and carbon dioxide. The general conclusion from these experiments is that the rate of distillation as governed by the vapor pressure of the solution is too slow to be practicable. It is not possible to heat the solution to a sufficiently high temperature to give a satisfactory current of vapor, since above 80° urea decomposes on continued heating in solution. It was very evident that some carrier for the gases must be provided to hasten the distillation at lower temperatures.

DISTILLATION WITH CARBON DIOXIDE—The selection of carbon dioxide as the carrier gas was largely due to its relative cost as compared with ammonia. Under the conditions of operation it seemed probable that a small fraction of the carrier gas would be lost, but the excess of carbon dioxide in the condenser would effect a higher percentage of ammonia utilization. Consequently, the use of carbon dioxide as a carrier gas is justified. In this connection it may be well to refer to the possibility of recirculating the gases coming out of the condenser instead of passing them into acid for the recovery of uncondensed ammonia. This recirculation would effect a saving of both carbon dioxide and ammonia, and deserves consideration. No attempt was made in this work to test out the practicability of recirculation.

In these distillation experiments, the apparatus was arranged so that carbon dioxide could be forced through the liquid sludge and then through the jacketed pipe leading to the condenser. A tube, connected to the vent in the hopper of the condenser and dipping into water, gave an indication of the volume of gas passing through the system without condensing. The flow of carbon dioxide was regulated so that this volume of escaping gas was very small. Several sludges were distilled in a stream of carbon dioxide and without adding any "make-up" ammonia in order to test the efficiency of the carrying agent. Results showed that all but a few per cent of the ammonia could be removed from the liquid sludge when carbon dioxide was used as a carrier and that complete condensation of the ammonia distilled off could be obtained under proper conditions. The rate of distillation and the smoothness of the heating curve of the sludge were found to be important factors bearing on the efficiency of condensation. The rate of distillation is of course governed by the capacity of the condenser. From Fig. VI we see that the maximum capacity at 100 per cent efficiency is about 700 g. per hr. The autoclave has a capacity of about 4500 g. in 4 hrs. or 1125 g. per hr.—very nearly twice the capacity of the condenser. It is to be expected that the preparation of an autoclave charge cannot therefore be efficiently carried out in 4 hrs. with the apparatus described. These experiments indicated that it was possible to condense completely the vapor distilling from a sludge.

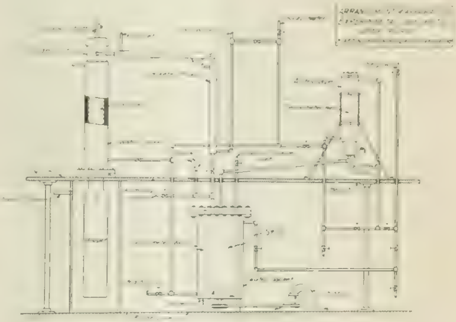

FIG. IX

The sludges have a boiling point, or region, where the distillation will proceed regularly and uniformly. If superheating is attempted it is to be expected that control of the flow of gas will be difficult. We have found that this boiling range is at about 57° to 59° C.; if this temperature is maintained throughout most of the distillation a steady stream of vapor can be passed into the condenser. When most of the gaseous constituents of the sludge have been distilled off it is necessary gradually to increase the temperature until about 80° C. is reached. With these results obtained, the final step of the investigation was to combine the use of the carrier and the addition of "make-up" ammonia.

It can be seen that continuous operation of this process is possible when the capacities of the autoclave and condenser are the same; that is, the condenser must produce during the period of conversion just as much ammonium carbamate as the autoclave requires for one charge. Since continuous operation is most economical because it avoids the intermittent heating and cooling of the autoclave, this object has been kept always in view.

DISTILLATION WITH CARBON DIOXIDE CARRIER AND "MAKE-UP" AMMONIA—A series of six distillations was performed in which the heating curves were strictly comparable, the volume of carrier approximately constant, and the rate of addition of "make-up" ammonia varied between wide limits. The time of distillation was limited to 4 hrs., and the operation with different rates of flow of ammonia studied. In these experiments the "make-up" ammonia was introduced into the stream of vapor coming from the sludge just as these vapors entered the jacketed pipe leading to the condenser.

The efficiency of condensation in this series varied from a little above 50 per cent to 82 per cent. High rates of flow, 7.84 l. of ammonia per min., caused the formation of a mist in the condenser which led to low efficiencies. The best efficiency was obtained with an ammonia flow of 3.95 l. per min. Attempts to operate the condenser at capacity were made. In one experiment, 4275 g. of condensate were formed in 4.2 hrs., at the rate of 1017 g. per hr. and with an efficiency of 73.8 per cent. This shows that even a small condenser such as we have used can be made to produce fairly large amounts of condensate at a sacrifice of efficiency. In commercial operation circumstances may make this permissible, especially when ammonia compounds such as nitrate, chloride, or sulfate are being produced at the same plant. The possibility of recirculation of the gases coming out of the condenser should be considered in this connection.

Recovery and Purification of Urea

After distillation, the sludge residue consists essentially of urea and water with small amounts of ammonia and carbon dioxide. Evaporation to dryness would normally yield fairly pure urea, since all other constituents are volatile. In these experiments, however, all iron surfaces were not protected from the action of the sludge, and, as a result, the urea contained several per cent of iron oxide. Practically pure urea was obtained by partial evaporation, filtration from iron hydroxide, and finally evaporation to dryness. A single recrystallization makes the material chemically pure. For fertilizer purposes direct evaporation of the sludge residue to dryness should suffice.

Résumé of Process

The synthesis of urea from ammonia and carbon dioxide as developed by the operation of a small experimental plant is as follows:

1—The original charge of ammonium carbamate is prepared by condensing a mixture of ammonia, carbon dioxide, and water vapor in a condenser provided with a rotating, scraping blade.

2—The carbamate charge is formed by means of pressure into briquets of such size as to fit easily into the autoclave, which is kept continuously at 150° C.

3—The briquetted charge of carbamate is placed in the hot autoclave and the conversion to urea is carried out at 150° C.

4—The converted charge (now liquid) is released slowly into a still and the unconverted ammonia and carbon dioxide distilled off and recondensed together with additional gas to re-form a new charge of carbamate.

Cost Considerations

The data obtained in the operation of our small experimental plant do not furnish a satisfactory basis for estimating the probable cost of commercial production of urea by this process. They do, however, serve to indicate in a general way its commercial possibilities.

As previously stated, the only materials required are ammonia and carbon dioxide. The cost of the ammonia is of course very important, and will depend on the market value of uncombined ammonia gas. Carbon dioxide is a waste product in a number of manufacturing processes and its cost will, therefore, largely depend on how advantageously the urea plant is located with respect to a suitable source of waste carbon dioxide. The operation of a urea plant in conjunction with a direct ammonia synthesis plant, using the water-gas reaction for hydrogen, would be particularly advantageous in that respect. Even regarding the process merely as a means of "fixing" ammonia for fertilizer use, carbonic acid has a number of decided advantages over sulfuric or hydrochloric acids, and, therefore, urea may command a premium over ammonium sulfate and ammonium chloride.

The equipment required for the process is comparatively simple but is of somewhat special design. As a result of the nature of the process, the units of a commercial plant will probably have to be comparatively small and for that reason the processing cost may be higher per ton of product than in certain other processes. The process is, however, quite simple.

The labor charges should not prove to be high in commercial operation of the process. The handling of the material can be made very largely mechanical and the control is essentially mechanical also.

From the information available, it may be concluded that the cost of ammonia will constitute the principal cost of urea made by this process. The process, therefore, unquestionably possesses important commercial possibilities.

Acknowledgment

Grateful acknowledgment is made to Drs. Richard C. Tolman, A. B. Lamb, Graham Edgar, and J. M. Braham for many helpful suggestions during the course of this work.

Civil Service Examination

The United States Civil Service Commission has announced an examination for civil service examiner (junior grade) on July 5, 1922, to fill positions under the Civil Service Commission, Washington, D. C., at $1000 to $1200 a year. The duties consist of the preparation and rating of the various technical, scientific, professional, and clerical examinations announced by the Civil Service Commission for filling vacancies in the field or departmental service of the Government, and conferring with the heads of departments or governmental agencies concerning vacancies and the requirements for satisfactorily filling them. Registers of eligibles will be established as follows: first, of those attaining an eligible average in the basic subjects, and, second, of those who attain an eligible average in the basic subjects and an eligible rating in the optional subjects. Competitors will be rated as follows: a discussion of at least 300 words on one of three topics, to be written in the examination room—40; general information—40; education, training, and experience—20. Applicants may be examined in not more than two of the following optional subjects, and must state in application in which they desire to be examined: geology, French, Spanish, Italian, German, theory of accounts, general law, economics, sociology, chemistry, physics, editing, and proofreading.

Investigation of Sands Used in Aluminium-Alloy Foundry Practice

The Bureau of Mines, as one of the governmental agencies directly coöperating in a general research of all foundry sands, organized by the American Foundrymen's Association and the National Research Council, is collecting data on sands for molds and cores in aluminium-alloy foundry practice.

There is pressing need of collated information on sands used in aluminium-alloy founding, and it is hoped, as a result of the investigation, to aid in disseminating knowledge on the subject. A questionnaire is being sent by the Bureau of Mines to aluminium-alloy foundries in the United States in order to obtain data to be used in the preparation of a report.

Studies in Wood Decay[1]

III—The Toxicity of Western Yellow Pine Crude Oil to *Lenzites Saepiaria Fries*

By Henry Schmitz

Laboratory of Forest Products, School of Forestry, University of Idaho, Moscow, Idaho

The low toxicity and high rate of evaporation of the crude oil from the distillation of Western yellow pine make it of little value as a general wood preservative. It may, however, be adapted to special uses, as in the manufacture of shingle stains, preservative paints, etc.

The toxicity has been determined with sawdust from three species of wood as culture media: lowland white fir, Douglas fir, and sugar maple. The toxic point varies slightly with the species of wood used.

It is suggested that an ideal way to determine the toxicity of wood preservatives to wood-destroying fungi would be to set up such a culture series as was used in this work, and to determine the actual decomposition of the wood as indicated by the loss in weight of the flasks. The disadvantage would be that at least three months would be necessary, during which a volatile preservative would evaporate considerably.

The petri dish method was also used in this investigation.

From time to time, this laboratory has received inquiries concerning the possibility of employing the oil obtained by the destructive distillation of Western yellow pine as a wood preservative. Since, also, it is shown in a recent publication coöperated in by this Laboratory[2] that the yield of this oil is approximately 53.0 gal. per cord, and since definite information concerning the toxicity of such oils to wood-destroying fungi does not seem to be generally available, the present piece of work was undertaken.

Any substance which is to be used as a wood preservative must have other important properties besides being toxic to the growth of wood-destroying fungi, but even though a substance may fulfil all these other requirements, its use will be limited if it is not toxic to wood-destroying fungi.

Production of Oil

The oil was produced by heating the wood directly in a small retort approximately 12 in. in diameter and 36 in. long. The vapors were led through a worm condenser, and the distillate was collected in a separatory funnel. After settling, the water was drawn off and the oil transferred to a storage container. The oil was used as collected, with no attempt at redistillation.

Physical Properties

Crude Western yellow pine oil is a heavy sirupy liquid, acid in reaction, and of sharp pungent odor. It much resembles crude petroleum in general appearance. This sample of oil gave the following analytical results:

Sp. gr. at 38°	1.0141
Per cent water	0.70

When it was fractionally distilled in a 200-cc., round-bottom, distillation flask with the side tube at the center of the neck, the following results were obtained:

Distillation Temperature	Per cent
150°	10.43
200°	15.55
250°	13.20
300°	11.07
Residue above 300°	49.57

Whenever the rate of distillation fell below four drops per minute, the temperature was raised to the next highest distillation temperature. This is at variance with the standard system advocated by the American Society for Testing Materials for the fractional distillation of coal-tar creosote. However, it seems to the writer that there is little in favor of employing the same system of fractional distillation for two substances so entirely different as coal-tar creosote and crude wood oil. The above distillation temperatures are not suggested as a standard method of analysis of a wood oil, but they seem rational for the present purpose. It is assumed that the 150° C. fraction will include the wood alcohol, water, acetic acid, etc., that the 150° to 200° C. will contain the terpenes, and that the higher fractions and the residue will contain the rosins and tars.

Toxicity of Western Yellow Pine Oil Added to Various Kinds of Sawdust

In a recent paper by Schmitz and Zeller,[3] the large discrepancies between a method employing nutrient agar and one employing sawdust as a culture medium are shown. In the present work, the exact method outlined in the previous paper was employed. Ethyl alcohol, in which the oil was entirely soluble, was used as the solvent. After impregnation, the sawdust was exposed to the air for 24 hrs. in order to allow the alcohol to evaporate. Five-gram samples were then placed in 8-oz. bottles. Before sterilization, the bottles were tightly plugged with steamed corks and the corks securely tied to prevent them from blowing out during the steaming process. Sterilization was effected by steaming for 1 hr. in an Arnold sterilizer. After sterilization, the corks were replaced by sterile cotton plugs and the flasks inoculated with *Lenzites saepiaria* in the usual manner. The cotton plugs were then covered with two thicknesses of paraffined tissue paper to avoid excessive evaporation from the flasks, the paper being secured by means of a rubber band.

Three series were prepared: one with lowland white fir (*Abies grandis*) sawdust, one with Douglas fir (*Pseudotsuga taxifolia*) sawdust, and the last with sugar maple (*Acer saccharum*) sawdust. Crude yellow pine oil was added in amounts to make the following percentage concentrations, based upon the air-dry weight of the sawdust: 0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, and 15. The culture flasks were kept under observation for 21 days and examined at frequent intervals in order to determine in which flasks and to what extent growth had taken place.

DETERMINATION OF TOXIC CONCENTRATION—In order that there may be no confusion as to how the toxic concentration, which is defined as the minimum percentage of the oil which will completely inhibit the growth of the fungus, is determined, this phase of the work is discussed in some detail.

In a culture series, it is found that the growth of the fungus in the control flasks and in flasks containing small amounts of preservative is relatively copious. With the aid of a hand lens, the mycelium can easily be seen on the inner surface of the flask. Placing the inoculum near the wall of the flask simplifies this observation. With an increase in the amount of preservative, growth of the fungus becomes less extensive, but can still be found permeating the sawdust. With a further increase in concentration of the preservative, the growth of the fungus is confined to the inoculum. This type of growth can usually be easily observed on the cut surfaces of the inoculum. Finally, a concentration of the preservative is reached where there is no growth, even from the inoculum. The lowest concentration where all growth is inhibited is considered to be the toxic concentration. If there is any doubt as to whether limited growth has taken place, the inoculum can be removed from the culture flask and the cut surfaces examined by means of a hand lens. With very little experience, it is quite easy to determine whether or not growth has taken place.

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[1] Received November 21, 1921.

[2] I. W. Cook, Henry Schmitz and Louis Grant, "The Availability of Western Wood Oils for Flotation Concentration," University of Idaho, *Bull.* **16**, No. 13 (1921), 1.

[3] This Journal, **13** (1921), 621.

It is undoubtedly true that actual decay may be inhibited at a lower concentration than that determined in the above manner. However, when growth is very limited, it is practically impossible to determine whether this growth is entirely from the inoculum or whether the mycelium is obtaining a part of its food material by actually decomposing the sawdust. The point at which no growth whatsoever takes place is sharp and definite and the personal factor in its determination is reduced to a minimum.

The toxic concentration (as above defined), based on the dry weight of sawdust, was found to be between 9 and 10 per cent when white fir sawdust was employed as the culture medium, between 10 and 11 per cent when Douglas fir sawdust was used, and between 11 and 12 per cent when hard maple was used. The determinations were checked and rechecked, and the same results were obtained in each case.

EVAPORATION OF OIL—The legitimate objection might be raised that by exposing the impregnated sawdust to the air for a period of 24 hrs. the more volatile fractions of the oil would evaporate. In order to determine the rate of evaporation of the oil from the sawdust when exposed to the air, 5-g. samples of the sawdust were impregnated with crude oil and the various fractions of the oil in the manner previously described. These samples were exposed to the air and weighed after a 24-hr. exposure. The average results of a duplicate series, after correcting for the moisture changes indicated by the control, are given in Table I.

TABLE I—RATE OF EVAPORATION OF CRUDE WESTERN YELLOW PINE OIL AND VARIOUS FRACTIONS OF THE OIL FROM IMPREGNATED DOUGLAS FIR SAWDUST

OIL	Loss in Weight Per cent after 24 Hrs. Exposure
Fraction below 150° C.	68
Between 150°–200° C.	42
Between 200°–250° C.	6
Between 250°–300° C.	0
Residue above 300° C.	0
Crude oil	9
Control (sawdust without addition of oil)	2

Since 9 per cent of the oil was lost by evaporation by exposing the impregnated sawdust to the air for 24 hrs., it is necessary to make a corresponding correction of the toxic concentration previously determined. The corrected toxic concentration would be between 8.2 and 9.1 per cent when lowland white fir sawdust was used as the culture medium, between 9.1 and 10.0 per cent when Douglas fir sawdust was used, and between 10.0 and 11.0 per cent when sugar maple sawdust was used. It is of course recognized that these figures would not represent the actual toxicity of the original oil since the more volatile portions would be lost by the sawdust being exposed to the air. This difficulty is not encountered in determining the toxicity of coal-tar creosote because little or no loss in weight occurs during this stage of the operation.

If the toxic concentrations were based upon the net weight of the sawdust (5 g. sawdust plus 25 g. distilled water) they would of course be much lower, namely, between 1.4 and 1.5 per cent for lowland white fir sawdust, between 1.5 and 1.7 per cent for Douglas fir sawdust, and between 1.7 and 1.8 per cent for sugar maple sawdust. It would appear to the writer, however, that it is far more rational to compute the toxic concentration on the dry weight of the sawdust.

The ideal way in which to determine the toxicity of wood preservatives to wood-destroying fungi would be to set up a culture series as above described and to determine the actual decomposition of the wood as indicated by a loss in weight of the individual culture flasks. There are, however, several decided disadvantages to such a method, the most important of which would be (1) that at least a 3-mo. incubation period would be necessary before reliable results could be obtained, and (2) with such substances as coal-tar creosote, wood tar or any other volatile substance, a loss in weight would occur during the final drying to constant weight, as the result of the evaporation of the substance. With nonvolatile substances such as zinc chloride, sodium fluoride, etc., this method can be used and is now being used in the laboratory, in connection with an investigation of the effects of "soil alkali" on the rate of decay of wood.

TOXICITY OF THE OIL WHEN ADDED TO NUTRIENT AGAR

In a recent paper, Humphrey and his associates[4] point out what they consider to be the advantages of the petri dish method for determining the toxicity of a wood preservative to wood-destroying fungi. While this method has certain advantages, it also has disadvantages, the most important of which, in the opinion of the writer, is that there is not of necessity any relation between the toxic concentration determined by this method and the toxic concentration when sawdust is used as the culture medium. Coal-tar creosote may be ten times as toxic when mixed with nutrient agar as it is when used in connection with sawdust, while wood tar may be only five times as toxic in the former case as in the latter case. These figures are not to be taken as absolute, but merely illustrative.

In order to show what relationship, if any, exists between the results obtained by the two methods the following experiment was made: 100 g. of yellow pine crude oil were exposed to the air in a beaker until a 9 per cent loss in weight occurred. This corresponds to the loss of the oil taking place during the exposure of the impregnated sawdust to the air.

A hard potato agar was prepared according to the formula:

Extract from	200 g. potato	Agar	40 g.
Glucose	20 g.	Distilled water	1000 cc.

Fifty-cc. samples of this medium were pipetted while hot into 125-cc. Erlenmeyer flasks, and the flasks and their contents were sterilized. After sterilization, the yellow pine crude oil was carefully added to the series to make the following percentage concentrations of the culture medium: 0.05, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.8, 1.0, 1.2, and 1.4.

The flasks were then vigorously shaken until the agar was about to jell. The stoppers were removed and the contents of each flask approximately equally divided into two sterile petri dishes. After the medium in the dishes had cooled, the plates were inoculated from plate cultures of *Lenzites saepiaria* in the usual manner. Duplicate series were prepared in each case.

The plates were placed in large empty desiccating dishes to prevent excessive drying and evaporation of the oil and incubated for 4 wks. at 24°. Under the conditions above described the toxic concentration was found to be between 0.5 and 0.6 per cent. From this, it is evident that Western yellow pine oil has only very limited toxic properties.

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[4] C. J. Humphrey, Ruth M. Fleming and E. Bateman, THIS JOURNAL, **13** (1921), 618.

Drying Oils from Petroleum and Other Products, Produced by Chlorination and Dechlorination[1]

By Henry A. Gardner and E. Bielouss

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The following investigations were undertaken with the object of developing a commercial process for the production of a drying oil from petroleum, which could be used in place of linseed oil in the manufacture of paints, linoleum, and printing inks, and in similar industries. The investigations, which have covered a long period of time, were successful from a production standpoint, and the product is now being produced on a semicommercial scale for experimental use. Its drying value is equal to that of raw linseed oil. It has, moreover, the peculiar property of polymerization to a solid, elastic mass when heated to high temperatures. It is also susceptible to vulcanization with sulfur chloride to form plastic products of interest. It may be compounded with rubber and similar plastic materials. Unfortunately the color is very dark, and until a method is found of eliminating the color, its use in paints will be limited to black and very dark colors. For the latter purpose its durability has not proved entirely equal to that of linseed oil, when subjected to exterior exposure. In general, however, good results have been obtained.

THE drying power of linseed oil is largely due to the absorption by the latter of oxygen through the instrumentality of the *double carbon bonds.* While polymerization of the unsaturated glycerides and coagulation of the oxidized glycerides may also play an important role in this process,[2] no evidence is at hand to show that the carboxyl group of the acid or the hydroxyl radical of the glycerol has any bearing on the drying of the oil film.

The problem of producing a drying oil from the abundant source of mineral oil could therefore find its solution in the preparation of *unsaturated* compounds from the natural oil. Theoretically, the following reactions are at the disposal of the research chemist for this purpose:

1—Dehydrogenation, *e. g.*, elimination of hydrogen from a saturated compound by the aid of metals at high temperature,[3] the reaction being a reversible one.

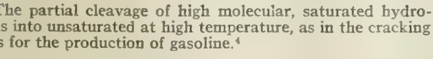
2—Elimination of water from compounds containing a hydroxyl group, as, for example, ethylene from ethyl alcohol:

$$C_2H_5OH \longrightarrow CH_2{=}CH_2$$

To this group belongs also the formation of unsaturated aldehydes by condensation of saturated ones, an aldol being primarily produced, for example:

$$2CH_3CHO \longrightarrow CH_3CH(OH)CH_2CHO \longrightarrow CH_3CH{=}CH.CHO$$

3—By electrolysis of a dibasic acid, as, for example, ethylene from potassium succinate:



$$\begin{matrix} CH_2COOK \\ | \\ CH_2COOK \end{matrix} + \begin{matrix} HOH \\ \\ HOH \end{matrix} \longrightarrow \begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix} + 2CO_2 + 2KOH + H_2$$

4—The partial cleavage of high molecular, saturated hydrocarbons into unsaturated at high temperature, as in the cracking process for the production of gasoline.[4]

5—The cleavage of halogen compounds by different methods into hydrogen halogens and unsaturated residue:

$$-CHCl-CH_2- \longrightarrow CH{=}CH- + HCl$$

The first four reactions are possibly not applicable for commercial purposes. The last was first made use of in the process of the De Bataafsche Petroleum Maatschappij.[5]

CHLORINATION

As a suitable source for the production of unsaturated hydrocarbons, several hundred types were experimented with. While successful results were obtained with a number of these, one of the best was a fraction known as nonviscous neutral oil. In the absence of any definite information as to its chemical composition, it may be assumed that it consists chiefly of the hydrocarbons $C_{17}H_{36}$ up to $C_{26}H_{54}$, the lower members of this range predominating.

A great many publications and patents are available on the subject of chlorination of lower and higher hydrocarbons of petroleum. The reactivity of the chlorine in the chlorinated hydrocarbons attracted the attention of many investigators in their desire to develop synthetic methods for the preparation of a number of industrially important products. Thus, Zilinski[6] chlorinated different fractions of Baku petroleum, subjecting[7] the products obtained to the Grignard reaction with the object of preparing fatty acids. C. F. Bochringer und Sohne[8] obtained resins by chlorination of petroleum. As a basis for the production of synthetic rubber, the Badische Anilin und Soda Fabrik[9] systematically chlorinated and dechlorinated pentane, with the conversion of the latter into isoprene. Brooks,[10] Oberfell, and Boyd[11] prepared amyl acetate from chloropentane. Methyl chloride, chloroform, carbon tetrachloride, etc., were prepared by chlorination of natural gas.[12] McElroy[13] has taken out a series of patents on the production of ethylene chlorohydrin by chlorination of ethylene. Dakin[14] is chlorinating paraffin, using the chlorinated product as a solvent vehicle for chloramine-T.

The methods applied for the direct chlorination by chlorine of paraffin hydrocarbons in the above and other processes all call for the aid of some catalytic agent in carrying out the absorption of chlorine. Water,[15] sulfur, phosphorus, iodine, carbon tetrachloride; metals or their oxides, as iron;[16] actinic light;[17] porous materials to increase the efficient concentration of chlorine;[18] sulfur dioxide, sulfur chloride and sulfuryl chloride,[19] and silent electric discharges[20] have been used.

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[1] Received April 26, 1922.

[2] P. Stransky, *Z. angew. Chem.*, **34** (1921), 86.

[3] M. Padra and U. Fabris, *J. Soc. Chem. Ind.*, **27** (1908), 1083.

[4] New Oil Refining Process Ltd., Brit. Patent 10,040, April 29, 1912. According to the claims in this patent, the unsaturated hydrocarbons formed can be utilized as siccative oils; see also Gawolowski, *Oesterr. chem. tech. Z.*, **70** (1910).

[5] Brit. Patent 23,376, December 1, 1914.

[6] *Z. angew. Chem.*, **16** (1903), 37.

[7] French Patent 326,665, November 25, 1902.

[8] D. R. P. 256,856, November 19, 1910; 258,156, December 28, 1911.

[9] French Patents 435,312, October 14, 1911; and 452,246, December 20, 1912

[10] THIS JOURNAL, **10** (1918), 511.

[11] U. S. Patent 1,302,583, May 6, 1919.

[12] Jones, Allison and Meighan, *Bur. Mines, Tech. Paper* **255**.

[13] U. S. Patents 1,253,615–17; 1,264,535; 1,295,339; 1,315,229.

[14] *J. Am. Med. Assoc.*, **69** (1917), 24.

[15] Bedford, U. S. Patent 1,245,553, uses water to remove the hydrochloric acid as fast as it is formed.

[16] *Ann.*, **225** (1884), 196; **231** (1885), 158.

[17] U. S. Patent 1,191,916.

[18] *Bur. Mines, Tech. Paper* **255**; U. S. Patent 1,380,067.

[19] U. S. Patent 1,362,355.

[20] U. S. Patent 1,012,149.

All these catalysts were tried out in our investigations. The writers found, however, that in the case of the neutral oils and other high boiling liquid paraffin hydrocarbons, the absorption of chlorine took place so smoothly at the temperatures employed that no catalyst was required.

The reaction involved in the chlorination of saturated hydrocarbons is one of substitution of hydrogen by the halogen, as evidenced by the following formula:

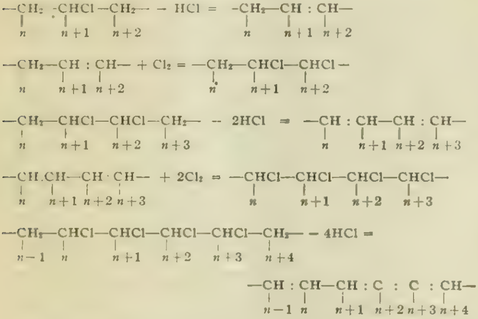
$$C_nH_{2n+2} + mCl_2 = C_nH_{2n+2-m}Cl_m + mHCl$$

As much chlorine is therefore evolved in the form of hydrogen chloride as is fixed by the hydrocarbon.

The following factors have a marked influence on the speed of this reaction:

VELOCITY OF CHLORINE—The chlorination is accelerated by the increase of the chlorine velocity up to a certain limit, while the coefficient of efficiency of the chlorine (Cl absorption: Cl input) decreases at the same time.

INFLUENCE OF TEMPERATURE—With rising temperature the absorption of chlorine is accelerated. This holds true for temperatures up to a certain limit. Above this point another set of reactions comes into play, especially when the chlorination has progressed for some time. The chlorinated hydrocarbon splits off hydrochloric acid, forming an olefin. The olefin would add chlorine, then by splitting off hydrochloric acid would yield a molecule containing conjugated double bonds. This molecule in its turn, by addition of chlorine and subsequent dechlorination, would result in an unsaturated compound of a quite unstable double-allenic structure. The following formulas illustrate this sequence of reactions:



$$—\underset{n}{\mathrm{CH_2}}—\underset{n+1}{\mathrm{CHCl}}—\underset{n+2}{\mathrm{CH_2}}— - \mathrm{HCl} = —\underset{n}{\mathrm{CH_2}}—\underset{n+1}{\mathrm{CH}} : \underset{n+2}{\mathrm{CH}}—$$

$$—\underset{n}{\mathrm{CH_2}}—\underset{n+1}{\mathrm{CH}} : \underset{n+2}{\mathrm{CH}}— + \mathrm{Cl_2} = —\underset{n}{\mathrm{CH_2}}—\underset{n+1}{\mathrm{CHCl}}—\underset{n+2}{\mathrm{CHCl}}—$$

$$—\underset{n}{\mathrm{CH_2}}—\underset{n+1}{\mathrm{CHCl}}—\underset{n+2}{\mathrm{CHCl}}—\underset{n+3}{\mathrm{CH_2}}— - 2\mathrm{HCl} = —\underset{n}{\mathrm{CH}} : \underset{n+1}{\mathrm{CH}}—\underset{n+2}{\mathrm{CH}} : \underset{n+3}{\mathrm{CH}}—$$

$$—\underset{n}{\mathrm{CH}}.\underset{n+1}{\mathrm{CH}}—\underset{n+2}{\mathrm{CH}}\cdot\underset{n+3}{\mathrm{CH}}— + 2\mathrm{Cl_2} = —\underset{n}{\mathrm{CHCl}}—\underset{n+1}{\mathrm{CHCl}}—\underset{n+2}{\mathrm{CHCl}}—\underset{n+3}{\mathrm{CHCl}}—$$

$$—\underset{n-1}{\mathrm{CH_2}}—\underset{n}{\mathrm{CHCl}}—\underset{n+1}{\mathrm{CHCl}}—\underset{n+2}{\mathrm{CHCl}}—\underset{n+3}{\mathrm{CHCl}}—\underset{n+4}{\mathrm{CH_2}}— - 4\mathrm{HCl} =$$

$$—\underset{n-1}{\mathrm{CH}} : \underset{n}{\mathrm{CH}}—\underset{n+1}{\mathrm{CH}} : \underset{n+2}{\mathrm{C}} : \underset{n+3}{\mathrm{C}} : \underset{n+4}{\mathrm{CH}}—$$

The possibilities of formation of a cyclic compound or isomerization through intramolecular transformation or migration is thereby left out of consideration.

INFLUENCE OF ABSORBED CHLORINE—In the first stage when the amount of absorbed chlorine is insufficient to transform the whole of the hydrocarbons into the monochloro derivative, it is the concentration of the hydrocarbon in the monochloro derivative which may influence the further chlorination. If we figure, for the sake of convenience, the *mean* molecular formula of our hydrocarbon mixture as $C_{20}H_{42}$, about 12.5 per cent increase in weight is necessary for the formation of the monochloro derivative. The numerous experiments of the writers showed that there is no marked change in the rate of absorption of the chlorine up to a 15 per cent absorbed chlorine (15 per cent increase in weight of the hydrocarbon). Above this point the absorption slows down considerably, this lowering of the absorption progressing continually with the increasing concentration of the polychloro derivatives. With progressing chlorination the velocity of chlorine has to decrease in order to keep the coefficient of chlorine efficiency (chlorine input: chlorine absorption) on the same level.

Dechlorination

The means for the removal of the hydrochloric acid from a chlorinated hydrocarbon can be divided into the following two main groups:

1—Dechlorination by the action of alkalies (usually in aqueous or alcoholic solution) on the halogen-containing hydrocarbons, whereby the liberated hydrochloric acid is *absorbed* by the alkali. Besides the formation of olefins, this reaction yields ethers and alcohols.[21]

2—Dechlorination by heating the chlorinated hydrocarbons to a temperature above their dissociation point, usually a number of catalysts being applied to facilitate this dissociation. Thus Sabatier[22] passed the chlorides over divalent metals at 260°. Senderens[23] used alumina for this purpose. A number of patents based on these methods were taken out by the Badische Anilin und Soda Fabrik[24] for the preparation of isoprene and its homologs.

In the course of these investigations it was found by the writers that in the case of the mixture of high molecular hydrocarbons, which is represented by the so-called neutral oils, *the dissociation point of the polychlorides lies between 120° and 250° C., and that by heating these chlorinated hydrocarbons up to 250° C., a practically complete dechlorination can be effected without the aid of any other agent.*

This dissociation of the chlorinated hydrocarbon does not necessarily lead to the formation of olefins. While a hydrocarbon containing 35 to 36 per cent of chlorine should yield after dechlorination (the degree of dechlorination was accurately determined by the titration of a standardized sodium hydroxide solution in which the hydrochloric acid evolved was absorbed) an olefin possessing a Hanus or Hübl number of 254, the iodine numbers always varied between 70 and 130. This phenomenon is due to the fact that olefins primarily formed undergo a further change in their nascent state, namely, transformation into cyclic compounds by a mutual saturation of their double linkages.[25]

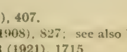
The unsaturated hydrocarbons obtained by the above process thus consisted of a mixture of open-chain olefins and of cyclic hydrocarbons of a presumably saturated nature. These hydrocarbons were investigated in their behavior toward the following reagents:

ACTION OF H_2SO_4—While the lower hydrocarbons give addition compounds with sulfuric acid, which through hydrolysis yield alcohols, the effect of this acid on our olefins consisted in a practically *complete* polymerization of the hydrocarbons; no water-soluble fraction could be extracted from the reaction product. The temperature range under which this reaction was tried was from −5° to +20° C.

ACTION OF S_2Cl_2—The action of sulfur chloride can be twofold: (1) Addition to the double-linked carbon atoms, and (2) substitution, mainly of the hydrogen, with disengagement of hydrochloric acid. By allowing the sulfur chlorides to act in small portions and keeping the temperature of the reaction mass low, it was possible to add the chloride in amounts of 10 per cent to 30 per cent of the hydrocarbons, with the formation of hard and brittle products. In the presence of at least 10 to 15 per cent of tung oil, rubber-like products were obtained, similar in appearance to certain of the so-called vulcanized oils.

ACTION OF HNO_3—Concentrated nitric acid acts very vigorously on the product, causing the formation of polymerized masses. It was found possible to prepare chloronitro hydrocarbons by slowly adding the chlorinated hydrocarbons to a mixture of 1 part HNO_3 (sp. gr. 1.42) to 4 parts H_2SO_4 (66° Bé.) and keeping the temperature fairly low. These chloronitro compounds contained from 3 to 4 per cent nitrogen.

ACTION OF ORGANIC ACIDS—Many unsaturated hydrocarbons are able to fix carboxylic acids at higher temperatures, with the formation of esters, as represented by the formula:



$$\underset{\mathrm{H}}{\mathrm{—C}} = \underset{\mathrm{O.CO.R}}{\mathrm{C—}}$$

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[21] *Ann.*, **318** (1901), 1.

[22] *Compt. rend.*, **138** (1904), 407.

[23] *Bull. soc. chem.*, [4] **3** (1908), 827; see also W. F. Faragher and F. H. Garner, *J. Am. Chem. Soc.*, **43** (1921), 1715.

[24] French Patents 435,312 and 434,586 (1911); D. R. P. 254,473 H and 255,538 (1913); U. S. Patent 1,221,382 (1917).

[25] Schaarschmidt and Thiele [*Ber.*, **53B** (1920), 2128–43] observed that by dechlorinating at higher temperatures chlorinated hydrocarbons of high molecular weight, the resulting olefins show a materially lower iodine number than those obtained by the action of alcoholic alkali.

No apparent change occurred by heating these olefins with acetic acid up to 120° to 130° C. for a period of 8 to 10 hrs. These olefins were heated with abietic acid up to 290° C. for 6 to 8 hrs. Although the acid number of the mixture was reduced from 80 to 5, no formation of esters took place, the resulting product consisting practically entirely of unsaturated hydrocarbons, as the abietic acid had split off carbon dioxide at the high reaction temperature.

CONCLUSIONS

1—By eliminating the presence of certain metallic compounds, it is possible to introduce chlorine into the mixtures of hydrocarbons represented by the so-called "neutral oils" and thereby evenly to distribute the halogen in the hydrocarbon molecule. The amount of chlorine which can be thus fixed by the hydrocarbons at certain temperatures is sufficient to form tri- and tetrachlorides.

2—The elimination of chlorine from the chlorinated hydrocarbons can be effected without the application of any catalytic or HCl-absorbing agent by heating the chlorinated compounds as high as 250° C. Under these conditions a *partial* saturation of the primarily formed double linkages takes place through formation of cyclic hydrocarbons.

3—It is believed that the products obtained from the above process will ultimately find wide commercial application.

4—The writers have also chlorinated and dechlorinated such semidrying oils as soy-bean and cottonseed oils, the resulting products having greatly improved drying properties.

Studies in Chrome Tanning[1,2]

Equilibria between Tetrachrome Collagen and Chrome Liquors. The Formation of Octachrome Collagen

By **Arthur W. Thomas**[3] and **Margaret W. Kelly**

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Measurement of the fixation of chrome by hide substance after 8.5-mo. contact with chrome liquors of various concentrations showed that maximum fixation occurred in a chrome liquor of a concentration of 1.5 g. Cr_2O_3 per 100 cc. of solution. The chrome collagen compound formed in this liquor proved to be an octachrome collagen, showing that the combining weight of collagen is as low as 94.

The changes taking place when tetrachrome collagen is in contact with chrome liquors over a similar time interval have been measured, showing that the formation of tetrachrome collagen is not strictly reversible.

The findings support the view that the "adsorption" of chromium from chrome liquors by collagen is a chemical reaction.

THE effect of concentration of chrome liquor upon the adsorption of its constituents by hide substance during the 48-hr. contact has previously been reported by the authors.[4]

The formation of a tetrachrome collagen was definitely established when 5 g. of hide substance (weight on dry basis) were rotated in contact with a chrome liquor containing 15.5 g. Cr_2O_3 per l. for 48 hrs. The purpose of the present experiments was to investigate the assumption that the formation of tetrachrome collagen is a reversible reaction. Since chromed hide powder does not lose any measurable amount of chromium upon several hours' washing, it was decided to allow tetrachrome collagen to remain in contact with solutions of varying chrome concentration for several months, before analysis.

While we were almost convinced that a tetrachrome collagen was the best we could hope for in the amount of chromium combined with hide substance, it was considered prudent to set up a concentration adsorption series to run the same length of time. Accordingly two sets of experiments were carried out as described below.

TETRACHROME COLLAGEN EQUILIBRIA

A sample of 112.5 g. of 1920 hide powder (equal to 100 g. dry substance) was treated with 4 l. of a commercial chrome liquor (concentration = 166.5 g. Cr_2O_3 per l.) for 72 hrs., when test showed that tetrachrome collagen had been prepared. The mixture was filtered through a cloth bag, washed with tap water, and then with distilled water until the washings showed the very faint test for sulfate which is characteristic of completely washed chromed hide powder. It was partly dried at 30° C., completed at 100°, and then spread out in contact with air at room temperature to come to equilibrium with atmospheric humidity.

Analysis showed: moisture, 10.41 per cent; Cr_2O_3, 10.01; SO_3, 8.25; and protein ($N \times 5.614$), 67.31. One gram of hide substance contained 122.5 mg. SO_3 and 148.7 mg. Cr_2O_3 (slightly above the tetrachrome value).

Portions of 7.286 g. (equal to 5 g. dry hide substance) each were placed in a series of twelve bottles, covered with 200-cc. portions of freshly prepared liquors, carefully sealed to prevent evaporation, set aside from October 21, 1920, to July 8, 1921, and shaken once a week. Duplicate portions of the solutions were set aside for the same interval. Analyses of the liquors are given in Table I.

TABLE I

		ORIGINAL LIQUOR		FILTRATE
LIQUOR	G. Cr_2O_3 per Liter	Log C_{H^+} October 21, 1920	Log C_{H^+} July 8, 1921	Log C_{H^+} July 8, 1921
1	0(H_2O)	....	....	−2.68
2	0.43	−3.45	−3.43	−3.22
3	3.01	−3.36	−3.24	−3.22
4	7.80	−3.35	−3.18	−3.17
5	15.36	−3.22	−3.19	−3.17
6	29.99	−3.19	−3.11	−3.12
7	51.15	−2.99	−3.00	....
8	79.03	−2.86	−2.86	....
9	112.2	−2.73	−2.79	−2.77
10	134.6	−2.60	−2.69	−2.66
11	151.8	−2.47	−2.63	−2.59
12	208.	−2.29	−2.32	−2.41

The results tabulated are shown graphically in Fig. 1 and will be discussed later.

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[1] Presented before the Section of Leather Chemistry at the 62nd Meeting of the American Chemical Society, New York, N. Y., September 6 to 10, 1921.

[2] Published as Contribution No. 386 from the Chemical Laboratories of Columbia University.

[3] Assistant Professor.

[4] THIS JOURNAL, **13** (1921), 31.

TABLE II—COMPOSITION OF CHROMED HIDE POWDER AFTER 8.5-MO. TREATMENT

(All figures on moisture-free basis)

SAMPLE	Protein Per cent	Cr_2O_3 Per cent	SO_3 Per cent	Mg. Cr_2O_3 per G. Protein	Mg. SO_3 per G. Protein
1	78.10	10.16	7.66	130	98
2	76.92	10.73	8.02	140	104
3	70.32	13.25	9.44	188	134
4	65.35	14.88	10.39	228	159
5	65.04	14.86	11.01	229	169
6	68.36	14.18	10.44	207	153
7	69.58	12.27	(10.26)	176	(148)
8	69.72	12.73	10.44	183	150
9	72.25	12.31	10.56	170	146
10	70.75	12.19	10.72	172	152
11	72.58	11.99	10.89	165	150
12	71.67	11.90	10.58	166	148

TABLE III—CHANGE IN COMPOSITION OF TETRACHROME COLLAGEN AFTER 8.5-MO. CONTACT

SAMPLE	Mg Cr_2O_3 per G. Protein Lost or Gained	Mg. SO_3 per G. Protein Lost or Gained
1	−19	−25
2	− 9	−18
3	+40	+12
4	+79	+36
5	+80	+47
6	+59	+30
7	+28	(+25)
8	+34	+27
9	+22	+24
10	+24	+29
11	+17	+27
12	+17	+25

8.5-MONTH ADSORPTION

Portions of hide powder equal to 5 g. dry substance were treated with 200-cc. portions of the identical liquors and under the same conditions as the tetrachrome collagen just described. They were set up on October 21, 1920, and filtered off July 7, 1921. It was desired to duplicate as well as possible the conditions employed by the writers[4] in a 48-hr. adsorption experiment in which 1918 hide powder was used. Since very little of the 1918 powder was available, and in anticipation of a possible variation due to the use of a later hide powder, the series was made completely with 1920 hide powder, but the first five concentrations were duplicated with 1918 powder.

Since the liquors were identical with those described in the first part of this paper, the only additional analytical data are the C_{H^+} of the filtrates from the 8.5-mo. adsorption (Table IV).

TABLE IV

LIQUOR	Log C_{H^+}	LIQUOR	Log C_{H^+}	LIQUOR	Log C_{H^+}
2 *a*[1]	([2])	5 *a*	−3.18	9	−2.85
2 *b*[1]	([2])	5 *b*	−3.27	10	....
3 *a*	−3.61	6 *a*	−3.11	11	−2.65
3 *b*	−3.56	6 *b*	−3.18	12	−2.45
4 *a*	−3.47	7	−2.97		
4 *b*	−3.37	8	−2.90		

[1] *a* refers to 1920 and *b* to 1918 hide powder.

[2] Samples had decomposed and hence were discarded.

TABLE V—COMPOSITION AFTER 8.5-MO. ADSORPTION

(All figures on dry basis)

SAMPLE	Protein Per cent	Cr_2O_3 Per cent	SO_3 Per cent	Mg. Cr_2O_3 per G. Protein	Mg. SO_3 per G. Protein[1]
3 *a*	79.81	9.56	7.06	120	83
3 *b*	81.05	9.07	7.22	112	83
4 *a*	68.69	14.36	9.59	209	134
4 *b*	70.20	13.87	9.91	198	135
5 *a*	63.68	16.94	10.80	266	164
5 *b*	64.91	17.29	10.99	266	163
6 *a*	68.95	13.85	10.41	201	146
6 *b*	69.38	14.53	10.70	209	148
7	72.10	12.00	10.08	166	135
8	72.81	11.02	9.99	151	132
9	74.08	10.58	9.81	143	127
10	74.59	10.11	9.64	136	124
11	77.40	9.13	9.00	118	111
12	88.89	4.03	5.35	45	55

[1] Corrected for S present in hide powder. The 1918 hide powder (*b* series) contained 0.62 per cent sulfur (dry basis calculated as SO_3), and the 1920 (*a* series), 0.53 per cent.

These results are graphically represented in Fig. 2.

For comparison with the 8.5-mo. curves, the 48-hr. picture of the concentration relationships, previously published, has been included in Fig. 2.

The striking feature brought out by these curves is the point of maximum obtained in the liquor containing 15.36 g. Cr_2O_3. This chromed hide substance is *octachrome* collagen, as calculated from the fact that it contains 26.6 g. Cr_2O_3 per 100 g. hide protein, checked by two batches of hide powder.

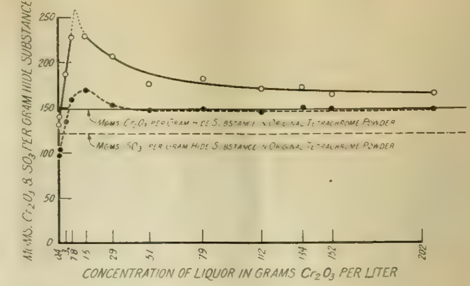

FIG. 1

In 1917 Wilson[5] gave 750 as the molecular weight, or as a multiple of the equivalent weight, of collagen, which was based on work by Procter[6] and by himself in Procter's laboratory. Using this value he calculated 3.38 g. Cr_2O_3 as the smallest amount to react in equivalent proportions with hide protein. Miss Baldwin[7] obtained a chromed collagen containing 13.4 g. Cr_2O_3 per 100 g. hide protein, which was approximately four times Wilson's minimum value. She stated that this was the greatest amount of Cr_2O_3 ever reported as capable of combining with collagen. From her values it followed that 187 could be regarded as the combining weight of collagen or hide protein.

Our result for octachrome collagen, obtained in the same concentration of liquor that gave tetrachrome collagen in 48 hrs., is a new record and shows the combining weight of collagen to be about 94. Another interesting feature is the point of inflection occurring between the liquors containing 112 g. and 134 g. per l. of Cr_2O_3, corresponding to tetrachrome collagen.

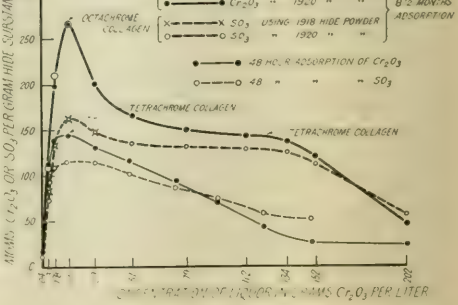

FIG. 2

Fig. 1, showing the changes taking place when tetrachrome collagen is in contact with different concentrations of liquors proves that in water, and in the most dilute liquor, a hydrolysis of the chrome collagen and collagen sulfate compounds took place, which is reflected also in an increase in the H-ion concentrations of the liquors. From that point there is a steady addition of SO_3 and of Cr_2O_3, approaching the octachrome collagen which was to be expected from the results obtained in the adsorption experiments; but while a considerable loss in chrome was to be expected in liquors containing over 29 g. Cr_2O_3 per l., in view of the steady fall in the 8.5-mo. adsorption curve, it is not so great as anticipated. In other words, the reaction in the concentrated liquors is not strictly reversible. This would indicate that the fall in the adsorption concentration curves is due to the effect of the increased H-ion concentration of the liquors, making the collagen more electropositive and more highly hydrated and thus inhibiting its combination with chrome, which is not possible with tetrachrome collagen since the nature of the collagen has been decidedly changed by chemical combination with the chromium.

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[5] *J. Am. Leather Chem. Assoc.*, **12** (1917), 108.

[6] *J. Chem. Soc.*, **105** (1914), 313.

[7] *J. Am. Leather Chem. Assoc.*, **14** (1919), 433.

These results lend extra support to our belief, previously stated,[4] that the combination of chrome with collagen is strictly a chemical reaction, and not a physical adsorption process.

ADDENDUM

As a precautionary measure, a duplicate of the tetrachrome equilibria and of the concentration series adsorption experiments were set up on April 29, 1921. After the values reported above in the 8.5-mo. series were obtained, it was considered of interest in the latter part of August 1921 to filter off these duplicate sets which represented about a 13-wk. contact, and compare the action with that of the experiments of longer duration of time. For brevity, details are omitted.

The values are not included on the graphs in order to avoid confusion, but if they were plotted it would be seen that the tetrachrome equilibria figures in Table VI are practically identical with those obtained after 8.5-mo. contact. This shows that the 8.5-mo. values represent in this instance an equilibrium that had been attained several months prior to the conclusion of the experiment. On the other hand, although the results given in Table VII follow the same shape of curve as those for 8.5-mo. reaction and closely approach the values set therein, they show one striking exception; namely, that the octachrome point was not reached in a 13-wk. reaction at room temperature, the maximum fixation of chrome being 239 mg. Cr_2O_3 per g. protein, as compared with 266 mg. Cr_2O_3 of the octachrome collagen found after an 8.5-mo. contact of hide powder with a chrome liquor containing about 1.5 g. Cr_2O_3 per 100 cc. of solution.

TABLE VI—CHANGE IN COMPOSITION OF TETRACHROME COLLAGEN IN CONTACT WITH CHROME LIQUORS FOR 13 WKS.

No.	Concentration of Original Liquor G. Cr_2O_3 per 100 Cc.	Mg. Cr_2O_3 per G. Protein Lost or Gained
1	0 (H_2O)	− 7
2	0.049	+ 7
3	0.190	+48
4	0.719	+73
5	1.469	+89
6	2.785	+47
7	4.617	+33
8	7.118	+26
9	10.64	+23
10	13.58	+27
11	14.95	+30

TABLE VII—COMPOSITION OF CHROME COLLAGEN RESULTING FROM 13-WK. CONTACT OF HIDE POWDER WITH VARIOUS CHROME LIQUORS

LIQUOR NO.[1]	Mg. Cr_2O_3 per G. Protein	LIQUOR NO.	Mg. Cr_2O_3 per G. Protein
2	Decomposed	7	164
3	111	8	149
4	196	9	141
5	239	10	133
6	197	11	113

[1] Concentrations given in Table VI.

ACKNOWLEDGMENT

We take pleasure in expressing our indebtedness to Messrs. A. F. Gallun & Sons Co., of Milwaukee, Wis., for their generous support of this investigation.

Pressure Bottle for Laboratory Use

By Arthur D. Hirshfelder and M. C. Hart

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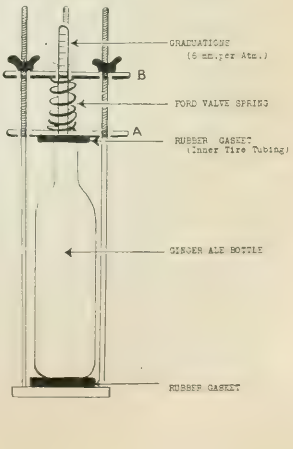
IN the course of experiments upon the preparation of aromatic alcohols, it was sometimes necessary to resort to syntheses under pressure at temperatures of about 150° C. On account of the pressures generated it was important that the vessel should have a safety valve. The authors adopted a modification of a pressure bottle which has been used in the chemical laboratory of the Johns Hopkins University. The apparatus used there consists of a pint ginger ale bottle held in a tripod frame. The mouth of the bottle is closed by a sheet rubber gasket pressed down by a brass plate, which is held in place by three wing nuts. In the modification of this apparatus the brass plate A surmounting the bottle is pressed down, not by nuts, but by means of a valve spring from a Ford automobile, the tension of which is regulated by a second brass plate, B, screwed down by wing nuts. A brass rod from the brass plate passes loosely through a hole in the upper brass plate and the tension of the spring can be regulated by the distance to which the upper plate is screwed down. In the case of ginger ale bottles with an aperture of about 20 cm., a compression of 6 mm. of the Ford valve spring corresponds to about 1 atmosphere of pressure. The brass rod is therefore graduated at intervals of 6 mm. (beginning at the point where the spring is not compressed at all), which correspond roughly to a scale of pressures in terms of atmospheres. The whole apparatus can be conveniently heated in an oil bath.

Several ordinary ginger ale bottles, *of the type with slightly convex bottoms*, which have been tested by Prof. F. B. Rowley of the College of Engineering of the University of Minnesota, have uniformly resisted a breaking pressure of 400 lbs. per sq. in. (more than 26 atmospheres).

The pressure bottle has worked very satisfactorily at temperatures of 150° to 160° C., and the valve pops off very well when set for 5 or 6 atmospheres. It should also be satisfactory for somewhat higher temperatures and pressures.



Estimation of Sulfate in Neoarsphenamine[1,2]

By Elias Elvove

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A method is described whereby the sulfate in neoarsphenamine can be determined without the preliminary precipitation, filtration, etc., of the formaldehyde sulfoxylic acid derivative of the arseno base which is called for by the method of Raiziss and Falkov. The results by the latter method, however, are higher than by the direct method, which increase is probably due to further oxidation to sulfate of sulfur present in lower stages of oxidation, during the preliminary precipitation, filtration, and washing of the precipitate. The direct method was used in determining the sulfate in thirty-four samples of neoarsphenamine from ten manufacturers. When calculated as Na_2SO_4, the results showed a variation from a minimum of 1.4 per cent to a maximum of 17.6 per cent. Averaging the results obtained with each manufacturer's samples separately these averages gave a minimum of 1.76 per cent and a maximum of 5.82 per cent. It appears, however, that the manufacturer can control his process so that his product will not vary very much in its sulfate content. Thus the average sulfate content (calculated as Na_2SO_4) of six samples of neoarsphenamine from one manufacturer was 3.52 per cent while, with the exception of only one sample, the largest difference was only 0.32 per cent; and including this one sample, the largest difference was only 0.73 per cent, although the samples examined cover a period of manufacture of about three years, during which time there were produced about six hundred and eighty-five different lot numbers.

A plan of procedure has recently been described by Raiziss and Falkov[3] for determining the distribution of sulfur in neoarsphenamine.[4] This procedure requires four gravimetric determinations, one of which aims to determine the sulfur which is present as sulfate in the original sample. This is carried out as follows:

> 0.3 g. of the neoarsphenamine is dissolved in about 25 cc. of water, the solution cooled in ice, and 5 cc. of dilute[5] hydrochloric acid are added. After standing 15 min. in the cold, the precipitate is filtered off quantitatively by suction through an asbestos and cotton filter[6] and washed many times with small amounts of 1 per cent hydrochloric acid. The filtrate, together with the combined washings, is then used for determining the sulfate by precipitation with barium chloride, etc.

In order to make it practicable to apply such tests in the routine examination of neoarsphenamine, it was thought desirable to simplify these determinations. As a result of some preliminary experiments, it was found that the determination of the sulfate can be carried out on the neoarsphenamine solution directly without the preliminary precipitation, filtration, and washing of the formaldehyde sulfoxylic acid derivative[7] of the arseno base. In addition to saving time and labor, this direct method appears to have also the advantage that it avoids the possible error which may result from further oxidation to sulfate of the sulfur present in lower stages of oxidation, during the preliminary treatment which is called for by the method of Raiziss and Falkov.

New Procedure

About 200 cc. of distilled water were boiled down to about 150 cc. in a beaker of about 400-cc. capacity. The boiling was stopped, but while the water was still hot (75° to 85° C.) a 0.2-g. sample of neoarsphenamine was added and quickly dissolved with the aid of a stirring rod. This was followed quickly by 10 cc.[8] of N HCl. The beaker was then covered with a watch glass and the contents boiled until the volume was reduced to about 50 cc. It was then diluted with distilled water to about 150 cc., heated to boiling, and to the gently boiling solution there were added slowly, from a pipet,[9] 15 cc. of 0.05 M $BaCl_2$. The precipitate of barium sulfate was allowed to settle over night and then was filtered and weighed.

Comparison with Results of Raiziss and Falkov Method

This procedure was applied to the determination of the sulfate in a number of commercial samples of neoarsphenamine. Some comparative results by this direct method and by that of Raiziss and Falkov are given in Table I.

TABLE I—COMPARATIVE RESULTS FOR SULFATE BY DIRECT METHOD AND AFTER PRELIMINARY PRECIPITATION

MANUFACTURER	LOT NO.	METHOD	Wt. of $BaSO_4$ Mg.	Difference Mg.
A	1	Direct	10.6	
		R. and F.[1]	26.8	16.2
A	2	Direct	10.5	
		R. and F.	26.8	16.3
B	1	Direct	7.9	
		R. and F.	19.2	11.3
B	2	Direct	7.6	
		R. and F.	20.3	12.7
C	1	Direct	6.6	
		R. and F.	24.8	18.2
C	2	Direct	57.9	
		R. and F.	64.1	6.2
D	1	Direct	5.5	
		R. and F.	20.7	15.2
D	2	Direct	6.4	
		R. and F.	17.5	11.1

[1] Preliminary precipitation, etc.

It will be noted that the amounts of sulfate found by this direct method are lower than the corresponding amounts found by the method of Raiziss and Falkov, which is in har-

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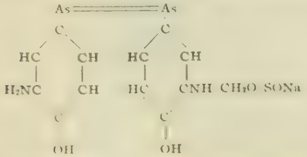
[1] Received March 21, 1922.

[2] Approved for publication by the Surgeon General.

[3] *J. Biol. Chem.*, **46** (1921), 209.

[4] In the literature, neoarsphenamine is usually given the formula.



It is now recognized, however, that the commercial neoarsphenamine is not the single chemical compound represented by the above formula but probably a mixture of this compound, a similar compound in which both amino groups have been combined with the formaldehyde sulfoxylate grouping, some uncombined sulfoxylate and various other impurities, the exact nature of which has not yet been determined.

[5] 2 N HCl was used in the determinations reported in this paper.

[6] *J. Biol. Chem.*, **18** (1914), 297.

[7] 3,3′-Diamino-4,4′-dihydroxyarsenobenzene-N-methylenesulfinic acid.

[8] Usually the precipitate which forms at first redissolves when the last portion of the acid has been added and the contents of the beaker mixed with the stirring rod. In the case of several samples, however, it was found necessary to add more than the 10 cc. of N HCl in order completely to redissolve the precipitate. In such cases, therefore, 20 cc. of the N HCl were added.

[9] The reason for using a comparatively dilute solution of barium chloride of known value was to facilitate the aim ultimately to carry out some of the sulfur determinations volumetrically.

mony with what we might expect, since the preliminary treatment (precipitation, filtration, etc.) called for by the latter method may increase the amount of sulfate through further oxidation to sulfate of the sulfur present in lower stages of oxidation, especially as it appears that the properties of this precipitate render its complete filtration and washing a comparatively very slow process.

ADDITION OF SULFATE

In order to prove that the lower results for sulfate by the direct method were not due to loss of sulfate caused by the preliminary boiling of the solution, known amounts of sulfate were added to some of the samples of neoarsphenamine which were used for obtaining the results given in Table I, and the total sulfate then determined by the direct method. The results obtained are given in Table II.

TABLE II—RESULTS BY DIRECT METHOD WITH SAMPLES OF NEOARSPHENAMINE TO WHICH KNOWN AMOUNTS OF SULFATE WERE ADDED

MANUFACTURER	Na_2SO_4 Added Grams	Weight of $BaSO_4$ Grams	Na_2SO_4 Equivalent Grams	Additional Na_2SO_4 Found Grams	Difference Grams
A	None	0.0106	0.0065	....	..
A	0.0142	0.0346	0.0211	0.0146	0.0004
A	0.0711	0.1269	0.0772	0.0707	-0.0004
B	None	0.0076	0.0046	....	....
B	0.0142	0.0304	0.0185	0.0139	-0.0003
B	0.0711	0.1226	0.0746	0.0700	-0.0011
C	None	0.0579	0.0352	....	....
C	0.0142	0.0797	0.0485	0.0133	-0.0009
C	0.0711	0.1731	0.1053	0.0701	-0.0010

The results given in Table II show that the added sulfate was recovered fairly quantitatively.[10] And although there seems to be a tendency for the results to be about a milligram or less under the true value, this, however, could not account for the very much greater differences (over 11 mg. in most cases) shown in Table I. This would indicate, therefore, that the higher results by the method of Raiziss and Falkov as compared with those obtained by the direct method are due to further oxidation to sulfate of the sulfur present in lower stages of oxidation, during the preliminary precipitation, filtration, etc., required by the former method.

TESTS OF METHOD ON PRODUCT FROM TEN MANUFACTURERS

Since it is now recognized that the commercial neoarsphenamine is not the single chemical compound which it had been represented to be, namely,[11] sodium 3,3′-diamino-4,4′-dihydroxy-arsenobenzene-N-methylenesulfinate, but that it is really a mixture of more or less varying composition, it appeared desirable to try out the direct method described in this paper on a comparatively large number of samples representing the products of as many different manufacturers as possible. The results obtained with thirty-four samples of neoarsphenamine from 10 manufacturers are given in Table III.

The results given in Table III show that the amounts of sulfate in commercial samples of neoarsphenamine vary considerably. Calculated as Na_2SO_4, it may be as low as 1.4 per cent (D, No. 4) or as high as 17.6 per cent (C, No. 2). The latter amount of sulfate, however, seems to be rather exceptional. But this variation is apparently not unavoidable, since some manufacturers (*e. g.*, A) produce a product which is fairly uniform[12] in its sulfate content. On the other hand, in the case of some other manufacturers (*e. g.*, C), the variation is comparatively very large. If we omit the results obtained with the samples from I and J, since there was only one sample of each examined, and average the results obtained with each manufacturer's samples separately, these averages give a minimum of 1.76 per cent and a maximum of 5.82 per cent. These figures, therefore, may be taken as indicating approximately the average limits of sulfate content when we consider the products of different manufacturers.

TABLE III—DETERMINATION OF SULFATE IN VARIOUS COMMERCIAL SAMPLES OF NEOARSPHENAMINE

MANUFACTURER	LOT NO.	PERCENTAGE Na_2SO_4	
A	1	3.25	
A	2	3.20	
A	3	3.45	
A	4	3.55	
A	5	3.45	
A	6	4.25	Av. 3.52
B	1	3.05	
B	2	2.40	
B	3	2.30	
B	4	3.75	
B	5	2.45	
B	6	2.30	Av. 2.71
C	1	2.00	
C	2	17.60	
C	3	1.75	
C	4	2.20	
C	5	3.45	
C	6	1.85	Av. 2.25[1]
D	1	1.70	
D	2	1.95	
D	3	2.00	
D	4	1.40	Av. 1.76
E	1	3.25	
E	2	2.65	
E	3	2.40	Av. 2.77
F	1	5.00	
F	2	2.85	
F	3	5.70	Av. 4.52
G	1	5.75	
G	2	5.90	Av. 5.82
H	1	3.30	
H	2	5.25	Av. 4.27
I	1	1.65	
J	1	4.20	

[1] Omitting Lot 2, which evidently contained a rather exceptionally large amount of sulfate.

While the primary object of the sulfate determination is to obtain figures which, together with other analytical data, will enable us to calculate the distribution of the sulfur in the neoarsphenamine, it would seem that it might also serve as a sort of partial index of the uniformity of the conditions of manufacture. Furthermore, although most of the sulfate can probably be traced to impurities in the sodium formaldehyde sulfoxylate, still it is quite possible that at least some of the sulfate, especially in the case of a manufacturer whose neoarsphenamine shows a comparatively large variation in its sulfate content, is the result of further oxidation to sulfate of sulfur present in lower stages of oxidation, during some stage of the process of manufacture or handling. And since when neoarsphenamine is partly oxidized it gives rise to a comparatively highly toxic[13] product and since conditions which will bring about such oxidation might also cause an increase of the sulfate content, it would seem that a comparatively large increase in the sulfate, which cannot be explained as due to extraneous sources, might be regarded with suspicion. The sulfate determination might, therefore, also serve for this purpose.

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[10] One might argue that the neoarsphenamine solution affects the solubility of the barium sulfate so that a certain amount of the barium sulfate is used up, in the case of the direct method, for saturating the solution. If this were so, one could recover quantitatively the added sulfate and yet not disprove the hypothesis that the direct method gives lower results for the reason that the introduction of the neoarsphenamine increases the solubility of the barium sulfate. In order to see whether there is any basis for such an argument, about 30 mg. of precipitated barium sulfate were added to a neoarsphenamine ("A," No. 1) solution of a concentration, acidity, and other conditions approximately similar to those which we have when the sulfate is determined by the direct method. The volume of about 150 cc. was boiled down to about 50 cc. It was then diluted again to about 150 cc., heated to boiling, allowed to settle, etc., just as in the case of the sulfate determination. Results showed that the introduction of the neoarsphenamine did not increase appreciably the solubility of the barium sulfate.

[11] Morgan, "Organic Compounds of Arsenic and Antimony," **1918**, 251.

[12] And in face of the fact that the samples tested cover a period of manufacture of about 3 yrs.

[13] Thus, for example, Roth [*Public Health Reports*, **35** (1920), 2205] found that shaking an aqueous solution of neoarsphenamine for 10 min. may increase its toxicity over fourfold.

The Surface Tension of Petroleum[1]

By C. K. Francis and H. T. Bennett

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The surface tension of petroleum from various sections of the United States has been determined. It is found that the value increases with the specific gravity.

The small quantity of fatty acids and amorphous and crystalline wax commonly found in petroleum products does not appear to influence the surface tension.

The presence of high boiling fractions and products of high viscosity tends to raise the surface tension of the lighter petroleum products, such as gasoline and naphtha.

The surface tension decreases as the temperature increases, the surface tension of the oils tested decreasing approximately 0.05 dynes per cm. for each °F. increase in temperature.

Surface tension in conjunction with other tests may aid in determining the lubricating and other values of an oil.

Many properties of oils are to be considered when studying their behavior in machinery, and these properties are important in connection with measurements of volume and transportation through pipe lines. No single characteristics may with reason and safety be chosen by which to judge an oil for a specific purpose, but a combination of properties is usually selected and an interpretation for value made from it. The addition of surface tension to the other commonly recognized properties of oils will, it is thought, aid in such an interpretation.

The facts presented in this article may, in themselves, appear to have a limited range of applicability, but it is thought that logical conclusions as to practical application may be derived from our experiments. The value of certain oils is concerned with the interface oil-metal, and better data would be contained in measurements showing the relation between liquid and solid.

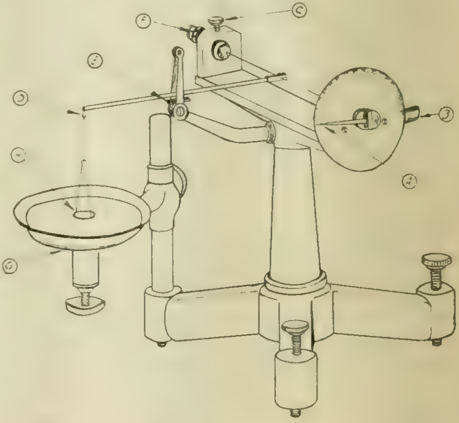
The surface tension of any liquid is due to the cohesive action of the particles composing the liquid. These cohesive forces act in all directions below the surface and a particle in the interior of a liquid is equally attracted on all sides, but a particle in the surface layer is attracted inwards by the particles of liquid within its sphere of influence, the corresponding attraction by the few particles in the vapor space being negligible in comparison. Hence, at the surface of every liquid there is a force, the so-called surface tension, which acts inward and causes the liquid to act as if it were covered by an elastic skin.

The surface tension of petroleum from different sections of the United States, and of the products derived from the various crudes, was determined in order to ascertain whether a relation existed between the surface tension and any other physical properties of the oils.

The measurements were made with the duNouy apparatus. The apparatus is simply a torsion balance, but instead of measuring the tension by means of weights, the torsion of wire is used to counteract the tension of the liquid film and to break it. A single reading on a dial supplies a figure from which, if the apparatus has been previously standardized with water, the surface tension may be obtained by a simple proportion.[2]

Method of Operating

The watch glass or beaker to be used for containing the liquid is thoroughly cleaned in a mixture of potassium bichromate and sulfuric acid, and then rinsed in distilled water. The liquid to be tested is then poured into the watch glass which is placed upon the table G in the accompanying figure. The platinum wire H is held in a flame until all organic material is burned. Then, without touching it with the fingers, it is hooked to the lever D. The needle indicator A is brought by means of the knob B just in front of the point O on the dial. Then, by using the adjusting screw F, the torsion of the wire is modified until the lever D is just above the resting platform E, the distance between them not exceeding the thickness of a piece of very thin paper. The screw C being fixed in position, one will observe that an imperceptible movement of the knob B will bring the lever in contact with platform E practically without changing the reading on the dial. The apparatus is now ready for use.



The table G is raised slowly by means of the adjusting screw until the liquid touches the platinum ring H. One must be sure that a perfect contact exists. Then, by turning the knob B the torsion of the wire is controlled, and one keeps on turning until the ring is suddenly separated from the liquid by tearing off of the film. The reading is then made. The average of the two or more readings is noted and the instrument is standardized as follows:

A small piece of clean paper is cut in such shape that it can easily be slipped upon the platinum ring H, in the stirrup, after it has been weighed. Weights are added on top of it, until the lever is forced down to its horizontal position, not quite in contact with the platform. It is now obvious that the sum of the weights, plus the weight of the paper, represents exactly in grams the strain of the wire. This being determined, we know the strain of the liquid film which was counteracted by the torsion of the wire. As the surface tension is expressed in dynes per cm., the number of grams must be multiplied by 981, and this product divided by the length of the circumference of the ring in order to have the number of dynes for every centimeter; but, as two films act on the ring, one outside and one inside, this result must be divided by two.

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[2] *J. Gen. Physiol.*, **1** (1919), 521.

$$\text{Surface tension in dynes per cm.} = \frac{M \times g}{2L}$$

where M = Weight in g.
g = Acceleration in cm per sec.
L = Length of platinum wire in cm.

Example

Water at 60° F.	
Weight necessary to bring lever down, grams	0.6260
Weight of paper, grams	0.0130
Total weight	0.6390

Then 0.6390 × 981 ÷ 8 = 78.357
Reading on dial 81

Then any reading on the dial, multiplied by the ratio 78.357/81 or 0.967, will give the surface tension in dynes of any liquid tested. The results may be checked to 0.2 dyne per cm. by this method.

EXPERIMENTAL

The surface tension of distilled water at different temperatures was determined, in order that comparisons could be made between the surface tension of oils and water at the same temperature, and that the duNouy figures could be compared with those obtained by any method.

TABLE I—SURFACE TENSION OF WATER

TEMPERATURE ° F.	SURFACE TENSION Dynes/Cm.
60	78.2
65	78.1
70	77.6
75	77.1
80	76.6
85	75.9
90	75.4

The surface tension and the gravity of petroleum were next determined.

TABLE II—SURFACE TENSION OF PETROLEUM FROM DIFFERENT FIELDS IN THE UNITED STATES

SOURCE	BASE OF OIL	COLOR	SPECIFIC GRAVITY	° BÉ.	SURFACE TENSION Dynes/Cm. at 85° F.
Cabin Creek, W. Va.	Paraffin	Yellow	0.7865	48.0	28.8
Winnette, Mont.	....	Very dark green	0.7937	46.4	29.0
Cushing, Okla.	Semi-paraffin	Very dark green	0.8279	39.1	29.7
Osage, Okla.	Semi-paraffin	Dark green	0.8403	36.6	30.7
Bixby, Okla.	Semi-paraffin	Very dark green	0.8444	35.8	30.8
Homer, La.	Semi-paraffin	Very dark green	0.8464	35.4	31.2

The results indicate that a relationship exists between the surface tension and the specific gravity of petroleum and that the former increases as the latter increases.

The physical constants of products from certain Oklahoma crudes were determined to ascertain the effect, if any, of gravity, volatility, and viscosity upon the surface tension.

The tests indicate that the surface tension increases as the Baumé gravity decreases and that the presence of high-boiling products increases the surface tension.

The surface tension appears to increase as the Saybolt viscosity increases, but the latter increases somewhat more rapidly than the former. The viscosity as determined by the Saybolt method is simply a measurement of the rate at which the oil will rise in a small capillary tube when under a slight pressure. As the surface tension is frequently determined by noting the height to which a column of liquid will rise in a small capillary tube, it would be expected that the Saybolt thermo viscometer readings would be affected by surface tension as well as by viscosity.

The results show also that the surface tension decreases as the temperature increases. It appears that the surface tension varies approximately 0.05 dyne per cm. for each ° F. change in temperature of the products tested.

TABLE III—TESTS ON LIGHTER FRACTIONS FROM PETROLEUM

Bé. Gravity	BOILING POINT, ° F. Initial	Max.	VISCOSITY[1] 60° F.	90° F.	SURFACE TENSION, DYNES PER CM. at ° F. 60	70	80	85	90
62.4	108	392		...		...		24.4	...
60.6	106	404	125	...	26.9	26.4	25.6		...
59.3	111	426	...	...	...	...	...	24.9	...
59.1	96	449	...	...	...	...	...	24.8	...
58.9	120	426	...	...	...	...	...	25.3	...
58.6	114	434	...	...	...	...	...	25.3	...
58.4	100	412	...	...	...	...	...	25.3	...
58.4	110	434	...	...	...	...	...	25.6	...
57.4	131	436	...	...				25.7	...
57.3	100	448	...	...	27.6	27.3	26.9		...
57.1	116	429	...	...	...	...	...	24.8	...
57.1	110	450		...		...		25.7	...
56.8	118	440	143	...	27.6	27.1	26.6		...
56.9	120	436	...	...	...	...	...	25.8	...
56.3	106	450		...		...		25.8	...
55.7	140	439	154	...	27.8	27.5	27.0		...
55.2	126	454	...	...	...	...	...	26.3	...
54.3	146	442	...	...	...	...	...	27.4	...
48.3[2]	132	558	...	...	...	...	...	28.2	...
46.7	224	466	...	...	...	...	...	29.2	...
45.9	146	608	249	...	30.0	29.5	29.0	...	...
43.9[2]	146	558						29.1	
42.2	326	490	320	247	31.9	31.9	30.9	...	30.5
41.5	344	575	419	312	32.7	31.9	31.2	...	30.9
39.5	380	612	545	396	33.1	32.4	31.9	...	31.4

[1] Viscosity determined with Saybolt Thermo Viscometer
[2] Cracked product.

As difficulty is sometimes experienced in pressing wax from wax distillate, on account of its poor crystalline structure, tests were made to ascertain if a relation existed between the surface tension and the crystalline structure of the wax in the distillates. The results are shown in Table IV.

TABLE IV—TESTS ON WAX DISTILLATE

Bé. Gravity	Flash	Fire	Cold Test	Crystalline Structure of Wax Present[1]	Viscosity at 100° F. Saybolt Universal	Surface Tension Dynes/Cm. at 85° F.
31.8	255	315	62	Fair	51	34.4
31.8	280	350	56	Fair	61	35.0
29.9	275	340	53	Fair	85	34.6
27.5	295	380	68	Fair	113	35.5
31.6	260	315	49	Poor	52	34.4
31.4	284	322	62	Poor	70	34.7
28.1	370	440	77	Poor	153	36.2
30.6	250	320	56	Good	57	35.0

[1] Determined by microscopic examination of the wax extracted from the wax distillate by shaking with chloroform, cooling, and centrifuging to remove the separated wax.

The wax was removed from two distillates, and the surface tension of the oil before and after the removal of the wax was determined. No difference was noted. The addition of 10 per cent of petrolatum, and 9 per cent of 122° melting-point wax also failed to change appreciably the surface tension. The above tests indicate that the surface tension test cannot be used as a guide for determination of the quantity and the crystalline structure of the wax in distillates.

The true relation between the surface tension and the lubricating value of an oil has not been determined, but it is evident that surface tension plays an important role in lubrication because it may aid in the maintenance of the oil film between the moving surfaces.

In order to study the relation between the surface tension and the properties of lubricants, tests were made on oils of different viscosities, on vegetable oil, and on a mixture of fatty acid and cylinder stock.

TABLE V—TESTS OF LUBRICANTS

PRODUCT	Bé. Gravity	Cold Test	Saybolt Universal Viscosity at 100°	Color N. P. A.	Surface Tension Dynes/Cm. 85° F
Oklahoma lubricating oil	27.1	23	155	2 –	36.0
Oklahoma lubricating oil	27.2	25	160	3 –	36.2
Oklahoma lubricating oil	26.2	26	185	4 –	36.0
Oklahoma lubricating oil	25.8	25	240	6 –	36.4
Oklahoma lubricating oil	25.5	19	260	Q +	37.5
Oklahoma cylinder stock	23.8	24	1160	Green	37.3
California lubricating oil	19.7	–0	428	4.5 –	37.3
Castor oil	15.9	10	100 at 210° F.	2	40.4

The above tests indicate that the great variations observed in the viscosity, the usual standard for determining the lubricating value of an oil, cannot be explained by the surface tension test of the oils as determined against air, because the differences in surface tension between viscous and comparatively nonviscous oils were slight. It appears that it would be necessary to measure the surface tension exerted at the interface between the oil and the metal, and not the surface tension of oil as determined against air, to determine the true relationship between surface tension and lubrication.

The addition of 1 to 5 per cent of fatty acids, that is, commercial oleic acid, soy-bean fatty acid, and animal fatty acid, to Oklahoma oils increased the surface tension very slightly, that is, 0.1 to 0.8, but not enough to signify any great change in the physical properties of the oil.

It is probably true that a dissolved substance changes the surface tension of a nonvolatile solution; therefore, it is reasonable to assume that foreign substances or impurities may exert considerable influence on the surface tension.

SUMMARY OF TESTS

PRODUCT	GRAVITY	SURFACE TENSION AT 85° F.
Crude	35.4 - 48.0	28.8 - 31.2
Gasoline	56.3 - 62.4	24.4 - 25.8
Naphtha	46.7 - 55.2	26.3 - 29.2
Kerosene	40.2 - 42.4	30.7 - 31.2
Gas oil	35.9	33.1
Lubricating oil	19.7 - 27.1	36.0 - 37.5
Wax distillate	27.5 - 33.2	33.6 - 36.2

Automatic Carbon Dioxide Indicator for Flue Gas[1]

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The accompanying diagram depicts an apparatus for the continuous automatic analysis of a gas mixture for one constituent, such as carbon dioxide in flue gas. The apparatus can be made with bottles and glass tubing, and can be assembled compactly in a wooden case, 8 in. × 20 in. × 20 in., provided with a window through which readings may be taken.

The instrument is accurate to 0.2 per cent carbon dioxide, and will record continuously for two days or more without need of refilling the scrubber or readjusting the zero point.

THE apparatus consists essentially of a dust trap, *c*, a differential flowmeter, *e*, the readings of which indicate directly the percentage of carbon dioxide, a Friedrich's spiral scrubber, *k*, containing 25 per cent sodium hydroxide, a control capillary, *m*, a device for maintaining a constant pressure drop around *m*, a device, *u*, for maintaining constant pressure drop around the entire system, and a suction pump, *y*.

The principle upon which the apparatus works is as follows: If a constant pressure drop be applied around the capillary *m*, air will be forced through it at a constant rate. If air, instead of flue gas, be sucked into the apparatus, the rate through the flowmeter *e* will be the same as the constant rate through *m*. This causes the indicating liquids in the manometer of the flowmeter to register 0 per cent carbon dioxide. If, now, gases containing carbon dioxide are sucked into the system, the caustic soda in the spiral scrubber causes enough additional gas to be sucked through *e* to make up the requisite standard rate of CO_2-free air through *m*. This increment of flow through *e* causes the indicating liquid in the manometer to be displaced by an amount corresponding to the per cent of carbon dioxide in the entering gas.

DESCRIPTION OF APPARATUS

DUST TRAP—An 8-oz. bottle filled loosely with cotton batting. Cock *a* admits flue gas and cock *b*, air to the system.

FLOWMETER—The capillary tube *e* is about 15 cm. long and of about 1-mm. bore. The bulbs g_1 and g_2 are taken from 50-cc. pipets and sealed to the manometric tubes h_1 and h_2, of 3-mm. bore and 35-cm. length.

The bulbs are filled half full of ethyl alcohol, colored with a dye. About 10 cc. of kerosene are placed in bulb g_1. The dye is insoluble in kerosene and the boundary between the two liquids is distinct. The specific gravity of the alcohol used was 0.805 and that of the kerosene was 0.790. While the boundary remains in the cylindrical part of the bulb g_1, a 1-cm. movement of the boundary will represent a 1.61-cm. head of water around the capillary *e*. In order to make the boundary sink just into the manometer tube h_1, a head of about 4 cm. alcohol or 3.2 cm. water is required. While the boundary is in the manometric arms a 1-cm. displacement corresponds to $0.805-0.790=0.015$ cm. water. Thus, the movement of the boundary in the arm h_1 is $1.61/0.015 = 108$ times as great as the movement in the bulb g_1 for the same increment of pressure.

The CO_2 scale placed behind the manometer must be determined by calibration. While air is being sucked through the instrument, the rate through the capillary *m* is varied until the boundary just sinks into the arm *h* to a level arbitrarily chosen as zero. Gas mixtures of known carbon dioxide content are next admitted to the system, and after equilibrium has been reached the displacement β is measured on a millimeter scale. These values of β are plotted against per cent of carbon dioxide as indicated in Fig. 2. The values of β corresponding to even percentages of carbon dioxide are marked on a strip of white paper which is to be fastened permanently behind the manometric arms.

If V_0 is the standard rate of gas flow through *m* and V_x, the rate through the flowmeter corresponding to *x* per cent carbon dioxide, the following relation holds:

$$100\,(V_x - V_0) = x.V_x$$

Inasmuch as the deflection β is very nearly directly proportional to the increment of rate (V_x-V_0) the spacing of the units on the CO_2 scale will be more liberal as the percentage of carbon dioxide increases.

The size of capillary chosen (1 mm.) gives a rate for V_0 of about 100 cc. per min. Cotton should be stuffed into the arms f_1 and f_2 to reduce and dampen the vibrations of the boundary due to bubbling in the system. This also prevents evaporation of the liquids used in the manometer.

SPIRAL SCRUBBER—A Friedrich's spiral scrubber will give intimate contact between the gas and the liquid, and assure complete absorption of carbon dioxide. The scrubber will have to be recharged with fresh sodium hydroxide periodically. If the flue gas contains 10 per cent carbon dioxide, 200 cc. of 25 per cent sodium hydroxide will last 55 hrs. before being converted to sodium bicarbonate:

$$\text{Time} = \frac{1.285 \times 25.5 \times 2 \times 22{,}300 \times 0.90}{40 \times 100 \times 60 \times 0.10} = 55 \text{ hrs.}$$

DEVICE FOR STANDARD RATE OF FLOW OF GAS—The capillary *m* is somewhat finer than that in the flowmeter. It should give a pressure drop of at least 15 cm. water for a

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[1] Received March 2, 1922.

[2] Research Chemist, Mathieson Alkali Works, Niagara Falls, N. Y.

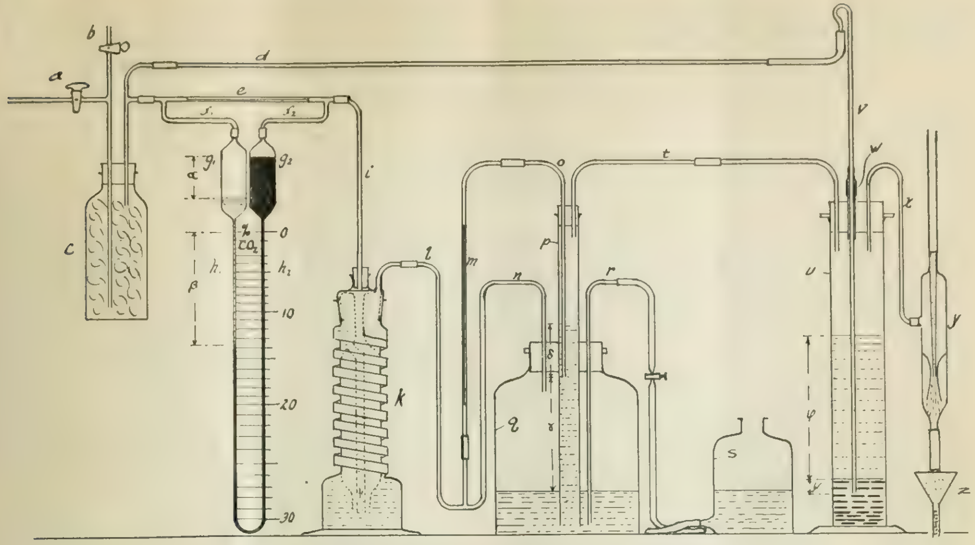

Fig. 1—Automatic Carbon Dioxide Indicator for Flue Gas

gas rate of 100 cc. per min. To facilitate selection and trial it is held in place by rubber nipples, as shown.

The wide-mouthed bottle *q* should be at least 13 cm. in diameter; its capacity is immaterial. The tube *p* is 1.3 cm. in diameter and 35 cm. long, and extends nearly to the bottom of the bottle. The 3-mm. tube *o* from the capillary extends to within about 18 cm. of the bottom of the bottle. Tube *t* connects the upper end of *p* with the suction device *u*. Liquid may be forced in or out of bottle *q* by means of the leveling bottle *s* and the siphon *r*. Tube *n* connects the pressure end of the capillary with the gas space in bottle *q*. Water may be used in *q* and *s*, but because of its tendency to evaporate and change the zero reading of the flowmeter, triacetin has been found better. It has an extremely low vapor pressure at ordinary temperature, is quite mobile, and is nonhygroscopic. It has a density of 1.160.

In operation, the suction on tube *t* is adjusted until the liquid level rises several centimeters above the outlet of tube *o*. The gas passing from *o* to *t* must therefore bubble through a column of liquid δ cm. high.

The pressure around capillary *m* is represented by the height of the liquid column γ. This remains constant, even for minor fluctuations in δ, because of the large cross-sectional area of the bottle *q* as compared to the tube *p*. For instance, a movement of 1 cm. in *p* corresponds to a change in γ of $(1.3/13)^2 = 0.01$ cm. A variation of 0.01 cm. when γ is 15 cm. corresponds to a change in head around *m* of 0.07 per cent. The head is adjusted by means of the leveling bottle until the flowmeter reads zero for air.

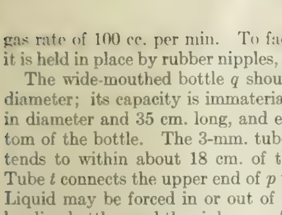

Fig. 2

CONSTANT SUCTION DEVICE—*u* is a hydrometer cylinder containing a several centimeter depth of mercury and about 10 cm. of water, or, preferably, triacetin. The open tube *v* slides through the rubber gland *w* and dips into the mercury. The outlet tube *x* connects with a small glass suction pump, *y*, actuated by water. The outlet tube on the pump should not be over 1 m. long. The pump is made to pull a small stream of gas down through tube *v* and through the liquid in *u*.

The upper end of *v* is connected to the dust trap by the tube *d*. By virtue of this connection, a constant head is maintained around the entire system. This head is represented by the depth to which tube *v* sinks into the mercury and triacetin. Thus ψ cm. mercury and φ cm. triacetin would correspond to a head of $13.6\,\psi + 1.160\,\phi$ cm. water. The tube *v* is adjusted until the liquid level in the tube *p* rises several centimeters above the outlet of tube *o* as indicated.

When the sample tube *a* is inserted in the chimney where the pressure is less than atmospheric, the seal in tube *p* might be broken, were it not for the equalizing effect of the by-pass *d*.

The flowmeter does not respond immediately to a change in per cent carbon dioxide. In fact, a sudden increase in the per cent carbon dioxide is always accompanied by a preliminary deflection in the wrong direction. This is because carbon dioxide is less viscous than air, and causes a decrement in pressure around the capillary *e* until this extra carbon dioxide begins to be absorbed by the sodium hydroxide in the scrubber. Two minutes should be allowed before reading, after a sudden change in the character of the gas sample.

The Department of Chemistry of the University of Maine will conduct a School of Chemistry and a Pulp and Paper School from June 26 to August 4, 1922. The work is designed to meet the specific needs of premedical students, teachers of chemistry and science teachers who wish to review the course in general chemistry or are preparing to teach chemistry, students who desire to begin or anticipate work in chemistry or make up deficiencies, students who are qualified to take pulp and paper courses, and pulp and paper mill men with or without technical training who have had practical experience and desire to gain a scientific understanding of important phases of pulp and paper manufacture and testing or phases of work with which they are unfamiliar. Special lectures on pulp and paper topics will be given.

Manufacture of Phosphoric Acid in the Electric Furnace by the Condensation and Electric Precipitation Method[1]

By Theodore Swann[2]

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The commercial production of phosphoric acid in the electric furnace by condensation and electrical precipitation is now being successfully conducted. Methods of purification have been worked out and are now in operation. Processes have been developed and are actually operating for the manufacture of various high-grade phosphate products.

PHOSPHORIC acid is one of the principal mineral acids used in agriculture and the industries. By far the largest portion is used in the fertilizer industry, but there has been a decided increase in its use for food products and numerous industrial purposes.

The method which has heretofore been generally used consists in treating a phosphate, usually bone or phosphate rock, with sulfuric acid. When the phosphoric acid has been converted into a soluble form, it is separated from the residue. Acid produced in this way is too dilute for many purposes and must be concentrated.

ELECTRICAL PRECIPITATION METHOD

Three furnaces are in full operation at Anniston, utilizing about 10,000 h. p. Electric power is supplied by the Alabama Power Company from its hydroelectric plant on the Coosa River and is delivered to the furnace transformers at 44,000 volts. Provision is made for varying the voltage in the furnace, as operating conditions may require.

Phosphate rock is obtained from Tennessee, though some Florida rock has been used; coke comes from the Birmingham district; and sand is available from local sources.

The process consists in charging a mixture of phosphate rock, coke, sand, and iron borings into an electric furnace, and smelting the charge so as to liberate the phosphorus in the phosphate rock. The iron absorbs a certain portion of the phosphorus and forms ferrophosphorus, which is tapped from the furnace. The lime and sand combine to form a slag, which is also tapped from the furnace. The ferrophosphorus analyzes from 24 to 25 per cent phosphorus, although the analysis may be varied depending on the grade desired. The phosphorus not absorbed by the iron passes through the charge together with the other furnace gases, which are oxidized by air and drawn out of the furnace into the condensing and precipitating apparatus. The acid as collected analyzes from 90 to 95 per cent H_3PO_4, is a light brown color, and has practically no suspended solids. A typical analysis is as follows:

	Per cent
H_3PO_4	90 to 95
Fe	0.06
$FePO_4 + AlPO_4$	0.39
CaO	0.04
SO_3	0.03
Pb	0.03
As_2O_3	0.02
F	0.01

The acid from the condenser and precipitator is treated for the removal of certain objectionable impurities. Special provisions must be made to prevent acid of this strength from crystallizing.

One of the outstanding features of the electric furnace condensation and precipitation method is the production of high-grade concentrated acid from phosphate rock containing a high percentage of iron. The process is new and differs from others which have been proposed in that it produces directly a high-grade concentrated acid and ferrophosphorus. Phosphate rock containing a high percentage of iron is not objectionable to this process, because the iron contained in the rock as well as that in the iron borings is removed as ferrophosphorus. Thus, an acid is produced which contains less iron than acid produced by the sulfuric acid method, even when the latter uses a phosphate rock containing a very low percentage of iron.

PURITY OF PRODUCT

The acid shipped is water-white, complies with all Federal and State Pure Food Laws, and is of approximately the following analysis:

	Per cent
H_3PO_4	75
Fe	0.05
$FePO_4 + AlPO_4$	0.30
CaO	0.01
SO_3	0.10
F	0.009
	P. p. m.
Pb	8
As_2O_3	0.5

Shipments are made in tank cars, barrels, and carboys. Tank car shipments have proved satisfactory. A wooden tank car is lined with a special wax compound that does not discolor the acid or affect its composition. Barrels are also lined with this compound.

Purified acid of this grade is used in producing high-grade salts for use in medicine. It is unnecessary to recrystallize to make a salt of exceptionally high purity. For instance, phosphate of soda has been made of a higher purity than any medicinal phosphate.

An acid of unusual purity can be prepared by crystallizing the acid from the condenser and precipitator. A U. S. P. 90 per cent H_3PO_4 has been made which, besides being suitable for all drug and pharmaceutical uses, is also adapted for the manufacture of hydrogen peroxide. Construction is now going on for a plant to produce high-grade acid in this manner.

Purified acid of 75 per cent grade is being regularly shipped as liquid phosphoric acid and is being used in the manufacture of phosphoric acid paste and crude monocalcium phosphate, for sugar refineries; in trisodium phosphate, for water softeners; in phosphate of soda, for textile uses. Equipment is being installed to make U. S. P. phosphate of soda, both anhydrous and crystals, monosodium phosphate, ammonium phosphate, and concentrated fertilizers.

APPLICATION TO FERTILIZER INDUSTRY

To obtain the maximum value of the developments which have just been described, this process must be applied to fertilizer production. The record of plant operation at Anniston during the past three years clearly indicates that with cheap hydroelectric power and proper plant location, phos-

[1] Address presented before General Meeting at the 63rd Meeting of the American Chemical Society, Birmingham, Ala., April 3 to 7, 1922.

[2] President, Federal Phosphorus Co.

phate rock can be smelted in the electric furnace for the production of fertilizer material at a cost comparing very favorably with the present methods. Fertilizer containing ammonia, phosphoric acid, and potash, having five times the amount of plant food contained in ordinary commercial fertilizers, have actually been produced at Anniston, and plans have been projected to develop larger scale operations.

This concentrated fertilizer will have the advantage of a great reduction in freights and a consequent saving to the farmer. It must be admitted that the farmer will be slow to adopt a concentrated fertilizer, but the reduced cost of such material will greatly influence him to utilize it.

In fixing the ammonia from either by-product coke-oven gas, the Haber, or other processes, phosphoric acid may be substituted for sulfuric and in this manner give two of the three essential elements of fertilizer.

Inasmuch as the largest consumption of fertilizers is in the South where the necessary raw materials, phosphate rock, coke, ammonia, and electric power, are all available, plants for the manufacture of concentrated fertilizer should be located here and such products economically utilized for southern agriculture.

Kellogg's Sampling Horn[1]

By James W. Kellogg[2]

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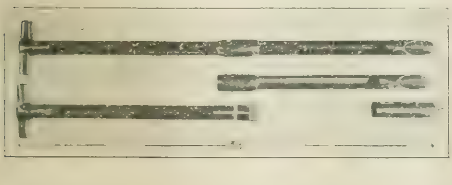
DURING the past fifteen years several types of sampling horns have been used by the Bureau of Chemistry of the Pennsylvania Department of Agriculture, for obtaining official samples of feedingstuffs and fertilizers for analysis. While it has been possible, with these horns, to obtain representative samples of these materials and thus secure results which were correct as far as the products were concerned, they were unsatisfactory in certain respects. They were too small or too great in diameter, cumbersome to carry, or difficult to empty and clean.

From a study of the efficiency of the types of horns in general use for official sampling work, it was concluded that an accurate and efficient horn should be just long enough to reach the bottom of the average sack, and have a bore, or inside diameter, of approximately 1 in., and should be made of such a gage or thickness of brass that it would not buckle or twist upon insertion in sacks. It should have a firmly attached handle, and a sharp-pointed, beveled open end, with an opening of such a size that the sample selected could be easily forced out with a spatula and the horn cleaned for further use. In order, therefore, to obtain these features, and especially to secure a compact instrument and to avoid the use of leather covers, a sampling horn has been designed, which has the features necessary in the accurate and correct sampling of both feedingstuffs and fertilizers.

DESCRIPTION

The new type of horn, as will be noted in the accompanying illustration, is in two sections or disjointed, making it possible for the operator to fold the two sections in a cloth and carry the horn complete in an ordinary sampling or suit case. The total length when joined is 31.5 in. The disconnected horn can therefore be placed in a sampling case with a 16-in. inside diameter. The upper section has a 4-in. handle securely fastened and the threaded end is protected with a screw cap. The lower section has a ferrule into which the upper section is screwed when in use and the beveled, sharpened knife edge point is protected with a slip-on cap. The outside diameter is $1^3/_{16}$ in., inside diameter, $1^1/_{16}$ in.; thickness of brass tubing used, $^1/_{16}$ in. The slots or openings, which are $^1/_2$ in. in width, are designed especially for removing the sample with a spatula. The left-hand edge (upper edge in illustration) is also sharpened, which aids in forcing the sample into the horn. It is so designed that when the lower section is held with the left hand, a right-hand turn, given to the upper section, joins both. When the horn is inserted in the sack the same right-hand turn is given, forcing the horn to the bottom of the sack. This operation at the same time forces the sample into the horn by means of the sharpened end or point and left-hand edges of the openings. This design has given very satisfactory results and overcomes the objectionable features of other types in general use.



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[1] Received April 20, 1922.

[2] Chief Chemist.

Review of Scientific Instruments

As announced in our January issue (page 85), the *Journal of the Optical Society and Review of Scientific Instruments* has begun publishing original articles and abstracts on scientific instruments of all kinds, electrical, mechanical, thermal, etc., for research, instruction, professional, and industrial work in all branches of science.

In order that this new department may grow as rapidly as possible it is desirable that any one who has apparatus to describe should submit it to that *Journal* for publication. The Editor-in-Chief is Mr. Paul D. Foote, Bureau of Standards, Washington, D. C.

International Congress on Liquid Fuels

The Société de Chimie Industrielle of France is organizing an International Congress on Liquid Fuels, to be held in Paris in October. This is being done in accordance with a desire expressed by the Hydrocarbons and Petroleum Section of the International Chemical Conference held in June of last year.

The two principal questions to be covered are the terminology of petroleum products and analytical methods. Sectional meetings will also be held under the headings: petroleum, oil shales, tar and benzene, and alcohols. An exposition will be held in connection with the Congress.

It is hoped that American fuel technologists will be adequately represented, in view of the extremely important position held by this country in that field.

Communications and requests for further information should be addressed to the Secretaire General, Mr. Jean Gerard, 49 Rue des Mathurins, Paris, France, and may be written in English.

Determination of Free Chlorine and Hypochlorous Acid in Concentrated Salt Solutions[1]

By **M. C. Taylor and C. A. Gammal**

THE MATHIESON ALKALI WORKS, INC., NIAGARA FALLS, N. Y.

The determination of free chlorine and hypochlorous acid in concentrated salt solutions which may contain either sodium hypochlorite or hydrochloric acid is comparatively easy if a physical method can be devised for obtaining the free chlorine. For this purpose an aeration process is usually employed, in which all the free chlorine driven out is assumed to have been originally present as such. However, in the case of brines containing appreciable amounts of hypochlorous acid, the chlorine obtained from the decomposition of this unstable acid during the course of the aeration makes it impossible to obtain even approximately accurate results.

In this paper it has been shown that the rate of removal of chlorine during aeration is approximately a linear function of the free chlorine content as long as any of that originally present as such still remains in the aeration vessel. After this point the rate of removal varies with the square of the hypochlorous acid present. Therefore the graph obtained by plotting the data on rate of chlorine removal will consist of two radically different sections, thus making it possible to obtain graphically an accurate estimate of the amount of chlorine originally present in the brine.

Details for the determination of hypochlorous acid and hydrochloric acid or sodium hypochlorite have also been given.

In connection with a research problem involving the electrolysis of sodium chloride, it became necessary to determine small amounts of hypochlorous acid and free chlorine in concentrated salt solutions which might contain either sodium hypochlorite or free hydrochloric acid.

De Mallman[2] outlines a method in which the free chlorine is determined by aeration of a 50- to 100-cc. sample for 5 min. However, no correction is made for the amount of free chlorine formed during the aeration process by the decomposition of hypochlorous acid, thus:

$$2HOCl + NaCl \rightleftharpoons NaOCl + Cl_2 + H_2O$$

Although the free chlorine formed in this way can probably be neglected when working with dilute salt solutions, the writers have found, as the above reaction would lead them to expect, that it can by no means be neglected when working with saturated solutions.

Clark and Iseley[3] give a method for determining free chlorine, hypochlorous acid and hydrochloric acid in chlorinated water which involves a titration of acidity with an organic indicator. But they themselves state that such a titration gives results that are inexact and difficult to duplicate. They also employ an aeration method for estimating free chlorine, in which they apparently correct for the hypochlorous acid decomposed by use of their inaccurate acid titration.

In the work reported herewith, the writers have developed a method which is a modification of the de Mallman procedure, in which they are able to correct accurately for the appreciable decomposition of hypochlorous acid occurring during the aeration of concentrated brine. Essentially the method involves three steps:

1—Determination of the "available" (free chlorine and chlorine as HOCl and NaOCl) chlorine in the sample with potassium iodide and thiosulfate, using a known excess of standard acid.

2—Determination of the excess acid remaining after the thiosulfate titration by titrating the iodine liberated from Kjeldahl's solution (a mixture of potassium iodate and iodide).

3—An aeration step in which the rate of washing over of free chlorine is accurately measured.

CHANGES OCCURRING DURING AERATION

The probable nature of the changes occurring during the aeration process is suggested by the following reactions:

For brines containing free hydrochloric acid:

$$HOCl \longrightarrow HCl + O \qquad (1)$$
$$HOCl + HCl \longrightarrow Cl_2 + H_2O \qquad (2)$$

For brines containing sodium hypochlorite:

$$NaOCl \longrightarrow NaCl + O \qquad (3)$$
$$2HOCl + NaCl \longrightarrow NaOCl + Cl_2 + H_2O \qquad (4)$$
$$3NaOCl \longrightarrow NaClO_3 + 2NaCl \qquad (5)$$

Having the methods of analysis outlined above in mind, it is evident that the occurrence of Reactions 1, 3, and 5 will cause a loss in total "available" chlorine and an *equivalent* gain in hydrochloric acid or loss of sodium hypochlorite. Furthermore, the occurrence of Reactions 2 and 4 will cause a change neither in "available" chlorine nor in acidity. In other words, the loss in "available" chlorine during aeration, expressed in cubic centimeters of thiosulfate, must always be equivalent to the increase in acidity expressed in the same manner, regardless of which of the above decompositions occur. The results show that this is the case within experimental error. This fact, together with other observations to be mentioned later, is taken to indicate that Reactions 2 and 4 are the only chlorine-producing reactions with which we have to deal.

The problem is, then, simply to determine the extent of Reaction 2 in acid brines, and of Reaction 4 in alkaline brines. This is done by a proper interpretation of the data on aeration.

INTERPRETATION OF AERATION DATA

The aeration process results in two actions:

1—Removal of the free chlorine originally present in the brine as such.

2—The removal of free chlorine formed by the decomposition of hypochlorous acid during or subsequent to the washing out of the original free chlorine.

If approximate values for the rate of washing out of chlorine at different stages in the aeration process are obtained by dividing the chlorine coming over during any period by the time and plotting these values as ordinates against the total chlorine washed over at the middle of that particular period as abscissae, two distinct curves result, as shown in Fig. 1. In the method herein described, the abscissa at the intersection of these two curves has been taken to be the free chlorine originally present as such. In order to justify this procedure the results obtained by its use, together with the aeration data, have been treated mathematically according to the prediction of theory, as set forth in the following paragraphs.

In the case of an "alkaline" brine where the only chlorine-producing reaction is represented by Reaction 4, we must regard the decomposing action as reversible as long as any free chlorine remains in the brine. However, when practically all the free chlorine has been removed by aeration,

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[1] Received April 25, 1922.

[2] *Compt. rend.*, **168** (1919), 1114.

[3] THIS JOURNAL, **12** (1920), 1119.

we may consider the decomposition as essentially irreversible, since the rate of removal of chlorine is very rapid as compared to its rate of formation. During the latter part of the aeration the removal of chlorine should proceed according to a bimolecular law, since in a concentrated brine the change in concentration of the sodium chloride can be neglected. For the rate of removal of free chlorine near the end of aeration, then, we may write:

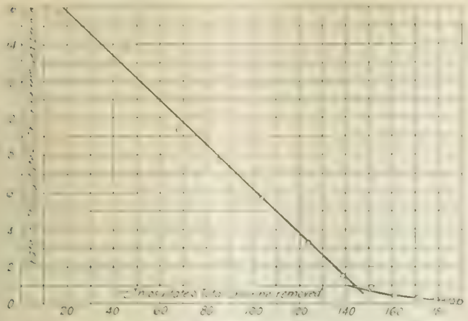

FIG. 1—TYPICAL GRAPH USED IN ESTIMATING FREE CHLORINE CONTENT OF A BRINE

$$\frac{dx}{dt} = K_1 (a - x)^2 \qquad \text{(I)}$$

where x is the chlorine washed over in t minutes, and a is the hypochlorous acid present at some time after the greater part of the original free chlorine has been removed. By assuming free chlorine absent at the close of aeration, making titrations similar to those outlined under (1) and (2) above on the brine remaining in the aeration vessel, we can determine the hypochlorous acid at the end. From this we can calculate the hypochlorous acid present at any time prior to the close of aeration and so evaluate a. Substitution in the integrated form of Equation I will give the values for "K bimolecular," tabulated in the two experiments of Table I. Comparison of the unimolecular K values obtained by substitution in the well-known unimolecular expression

$$K = \frac{1}{t} \log_e \frac{a}{a-x}$$

with the bimolecular constants can leave no doubt that the action is essentially bimolecular.

TABLE I—CALCULATION OF CONSTANTS

Time from Start Min.	Thiosulfate ⇌ Total Cl Washed over Cc.	Calculation of K t Min.	 a Cc. $Na_2S_2O_3$	 $a-x$ Cc. $Na_2S_2O_3$	 K Unimol.	 K Bimol.
			Analysis 4 (see Table II)			
59	166.1	20	56.8	47.9	0.0085	0.000164
89	175.7	50	56.8	38.3	0.0079	0.000170
119	182.1	80	56.8	31.9	0.0072	0.000172
140	185.7	101	56.8	28.3	0.0069	0.000175
155	187.3	116	56.8	26.7	0.0065	0.000171
170	189.1	131	56.8	24.9	0.0063	0.000172
185	189.8	146	56.8	24.2	0.0058	0.000163
			Analysis 7 (see Table II)			
112	512.5	60	399.4	296.5	0.0050	0.0000145
127	528.6	75	399.4	280.4	0.0047	0.0000142
142	545.6	90	399.4	263.4	0.0046	0.0000144
157	559.7	105	399.4	249.3	0.0045	0.0000144
172	571.8	120	399.4	237.2	0.0043	0.0000142
187	583.0	135	399.4	226.0	0.0042	0.0000142

During the first part of the aeration the rate of removal of free chlorine would be proportional to the amount present. If this amount was not being altered by formation of free chlorine from hypochlorous acid the rate could be represented thus:

$$\frac{dy}{dt} = K_2 (b - y) \qquad \text{(II)}$$

where y is the chlorine washed over in t minutes and b is the amount originally present. However, since chlorine is being formed from hypochlorous acid, the observed value will not coincide with such a linear relation as Equation II. If the brine be considered practically at equilibrium at the start of aeration the chlorine formed from hypochlorous acid, that is, the chlorine produced by the forward Reaction 4, minus that consumed by its reverse, will be very small until the free chlorine present has been reduced to a small amount by the aeration process. The chlorine formed from hypochlorous acid will be at a maximum at the intersection point of the two curves. Owing to the difficulties in obtaining these small corrections for formation of free chlorine, the K values of Equation II have not been given. However, from Fig. 1 it may be seen that the uncorrected observed values lie nearly in a straight line. It should be noted here that the value for the free chlorine originally present, obtained by the graphical method used, is not affected by the free chlorine which may have been formed from hypochlorous acid prior to the intersection point of the two curves.

An interpretation of aeration data similar to the above can be applied also in the case of acid brines where the chlorine-producing reaction is represented by Reaction 2.

The above considerations demonstrate the change in the character of the action which occurs when free chlorine originally present as such has all been removed, and thus justify the graphical methods used throughout this work.

APPARATUS AND DETAILS OF THE METHOD

The apparatus consists simply of a flowmeter for maintaining a steady flow of air, connected to a series of gas washing bottles. The first washer contains caustic for removing carbon dioxide; the second contains the brine being analyzed; the third and fourth contain potassium iodide for absorption of chlorine and are both attached to a 2-way stopcock in such a way that the effluent air from the aeration bottle can be made to pass first through one and then the other, thus making it possible to determine the rate of washing over of chlorine accurately without altering the speed of aeration.

Large experimental errors will be made unless care is taken in sampling. In the method used and recommended, a siphon was placed in the bottle of brine to be analyzed (the siphon reaching to within 2 in. of the bottom of the bottle) and about 50 cc. of solution were drawn off to make sure that no free chlorine was trapped in the siphon. Fifty cc. of standard (0.02 N) sulfuric acid and 50 cc. of neutral potassium iodide (10 per cent solution) were measured into two 200-cc. volumetric flasks. Samples of the brine to be analyzed were drawn—the first into one of the volumetric flasks, another into the aeration flask (200-cc. sample), and the third into the other volumetric flask. In filling the volumetric flasks the mouth of the siphon was kept under the surface of the potassium iodide and acid mixture so as to prevent loss of free chlorine.

The duplicate samples in the volumetric flasks were titrated with thiosulfate to the end-point; then 50 cc. of Kjeldahl's solution (5 g. potassium iodate and 30 g. potassium iodide in 1 liter of solution) were added and the liberated iodine titrated with thiosulfate. As carbon dioxide reacts quantitatively with Kjeldahl's solution, the titration should be done in Erlenmeyer flasks as rapidly and with as little shaking as possible. The other sample was aerated, the chlorine being trapped in first one wash bottle and then the other, and titrated with thiosulfate. The length of time of aeration depended on the nature of the brine. The potassium iodide used for chlorine absorption was made slightly acid with 0.02 N sulfuric acid at time of using. At the end of the aeration samples of the brine were taken in 200-cc. flasks containing potassium iodide and acid in the same amounts as before aeration and the same titrations made.

CALCULATION OF RESULTS

A determination made by use of the principles outlined above will involve the observation of data which we may symbolize as follows:

Let $\frac{a}{0.0355}$ = Cc. N $Na_2S_2O_3$ equivalent to total "available" chlorine in original sample.

$\frac{b}{0.0355}$ = Cc. N $Na_2S_2O_3$ equivalent to free chlorine washed over.

$\frac{c}{0.0355}$ = Cc. N $Na_2S_2O_3$ equivalent to "available" chlorine in sample at end of aeration.

$\frac{d}{0.0355}$ = Cc. N $Na_2S_2O_3$ equivalent to the acid used up in initial iodate titration.

$\frac{e}{0.0355}$ = Cc. N $Na_2S_2O_3$ equivalent to the acid used up in the iodate titration made after aeration.

$\frac{f}{0.0355}$ = Cc. N $Na_2S_2O_3$ equivalent to the chlorine formed during aeration process and washed over. This f corresponds to the free chlorine obtained after the intersection of the two curves in Fig. 1. These curves are obtained for each analysis by plotting the aeration data as explained above.

Also let x = Grams of chlorine present in original brine as free chlorine.

y = Grams of chlorine present in original brine as hypochlorous acid.

z = Grams of chlorine present in original brine as sodium hypochlorite.

u = Grams of chlorine present in original brine as hydrochloric acid.

It is assumed that hydrochloric acid and sodium hypochlorite cannot be present simultaneously in a brine. Keeping in mind the methods of analysis used it is evident that the following relations hold:

1—*For alkaline brines, i. e.*, those containing sodium hypochlorite.

$$x = b - f \qquad (1)$$
$$x + 2y + 2z = a \qquad (2)$$
$$y + 2z = d \qquad (3)$$

Solving these equations we find

$$x = b - f$$
$$y = a + f - d - b$$
$$z = {}^1/_2\,(2d - a + b - f)$$

2—*For acid brines, i. e.*, those containing hydrochloric acid.

$$x = b - f \qquad (4)$$
$$x + 2y = a \qquad (5)$$
$$y - u = d \qquad (6)$$

Solving these equations we find

$$x = b - f$$
$$y = {}^1/_2\,(a - b + f)$$
$$u = {}^1/_2\,(a - 2d - b + f)$$

As mentioned above, the loss of available chlorine during aeration must always be equal to the increase in acidity. Therefore:

$$a - b - c = d - e$$

Substituting these values for the knowns in the above equations, we obtain

1—*For alkaline brines.*

$$x = a - c - d + e - f$$
$$y = f - e + c$$
$$z = {}^1/_2\,(d + e - c - f)$$

2—*For acid brines.*

$$x = a - c - d + e - f$$
$$y = {}^1/_2\,(d - e + c + f)$$
$$u = {}^1/_2\,(c - d - e + f)$$

Thus, we have two methods of calculation, according as we do or do not use the b value. As this value is the sum of a large number of titrations, the experimental error is probably great and the writers prefer not to use it. It is thought that the accuracy of the experimental data can be judged by observing how closely the "$d - e$" value agrees with the "$a - b - c$" value.

RESULTS OBTAINED AND ACCURACY OF METHOD

Results typical of those obtained by the method described herein are given in Table II. The agreement between the "$a - b - c$" and the "$d - e$" values is satisfactory in nearly all cases. Also it should be noted that it is possible to obtain checking results in two altogether independent analyses on the same brine.

TABLE II

Analysis No.	$a - b - c$ Cc. $Na_2S_2O_3$	$d - e$ Cc. $Na_2S_2O_3$	COMPOSITION GRAMS/LITER HCl	HOCl	NaOCl	Cl_2
1a[1]	29.7	33.4	...	0.214	0.048	0.306
1b	26.6	29.0	...	0.206	0.054	0.312
2a	30.9	13.2	0.006	0.137	...	0.578
2b	17.9	20.4	0.014	0.149	...	0.562
3a	1.8	0.1	...	0.194	0.001	0.502
3b	2.7	0.5	0.005	0.203	...	0.496
4	18.5	17.6	...	0.179	0.034	0.262
5	5.2	4.3	...	0.008	0.010	0.036
6	21.4	19.0	...	0.187	0.054	0.400
7	191.0	214.5	...	1.490	0.139	0.385
8	17.3	14.5	...	0.228	0.009	0.507
9	32.5	27.1	...	0.314	0.013	0.830
10	7.9	8.4	...	0.387	0.036	0.338
11	11.5	8.5	...	0.238	0.028	0.310

[1] The *a* and *b* analyses are duplicates on the same brine.

A value for $(x + y)$ was obtained by altogether different chemical reactions than were employed above, as follows: A 100-cc. sample of the brine was treated with a known excess of sodium hydroxide, thus converting all "available" chlorine eventually to hypochlorite, according to the reactions

$$Cl_2 + 2NaOH \longrightarrow NaOCl + NaCl + H_2O$$
$$HOCl + NaOH \longrightarrow NaOCl + H_2O$$

The sodium hypochlorite was destroyed with hydrogen peroxide, the excess peroxide destroyed by boiling, and the residual alkali titrated. The alkali used up can be calculated. Let this be represented by g. Then, using the same symbols employed above, for alkaline brines,

$$x + y = g$$

and for acid brines

$$x + y + u = g.$$

Now these relations of the unknowns can be obtained by subtracting Equations 2 and 3 above for alkaline brines, giving

$$x + y = a - d$$

and for acid brines, by subtracting (5) and (6), giving

$$x + y + u = a - d.$$

Thus, in any case

$$a - d = g.$$

The results for three analyses are given in Table III. The agreement is satisfactory, within experimental error.

TABLE III

Analysis No.	$a - d$	g
6	296.6	295.2
12	425.8	423.5
7	785.4	788.0

In order to determine whether or not hypochlorous acid was washed over as such during the aeration process, the potassium iodide used to absorb the chlorine was tested for alkali after titrating the liberated iodine. The amount of alkali found was practically equal to the amount of alkali originally present in the potassium iodide. Even if air be passed through a solution of hypochlorous acid, made by distilling a chlorinated soda-ash solution, the amount of alkali found is not increased appreciably above the blank. The authors conclude that hypochlorous acid cannot be washed over as such. However, if the potassium iodide is alkaline the figure obtained for free chlorine will be low, due to the formation of hypochlorite or hypoiodite. Therefore the solution of potassium iodide employed for chlorine absorption was made neutral or acid with sulfuric acid when used.

ACKNOWLEDGMENT

The authors wish to acknowledge the helpful suggestions received during the course of this work from Mr. R. E. Gegenheimer, Chief Chemist.

Benzene as a Motor Fuel[1]

By J. J. Lawton

SYRACUSE, NEW YORK

THE demand for motor fuel is rapidly increasing from year to year, not only are the world petroleum fields becoming gradually exhausted, but we also have, in the opinion of eminent geologists, to look forward to the time when naturally occurring motor spirit will either be nonexistent or, at best, so expensive in production as to prohibit its practical use. In the year of 1919 the world's consumption of crude petroleum equaled 558,692,519 bbls., of which the United States consumed 377,719,000 bbls.

It has been proved beyond the slightest doubt that benzene is an excellent fuel for the internal combustion motor. As long ago as 1907 attention was called by the *Motor Union* to the use of benzene as a motor fuel. Those were the days when petrol was a vastly superior fuel to that at present obtainable, which is a much heavier spirit owing to the inclusion in it of a larger proportion of the higher boiling fractions of the crude petroleum. "On the other hand, cars and engines have greatly improved in design since 1907. Many of these improvements, and particularly the almost universal substitution of the spray carburetor for that of the evaporative type, facilitate the use of a much more varying class of fuel in the same engine, with little or no adjustment." In fact it may truly be said that any modern and efficient petrol engine will consume benzene quite as efficiently, the change being made practically without trouble or expense.

Sir Dugald Clark, an authority on this subject, gives the requirements of a suitable motor fuel as follows:

EASY STARTING FROM COLD—The ease of starting depends on the volatility and vapor pressure of the fuel, and it may be stated here that although benzene is far less volatile than gasoline of six to eight years ago, the advantage which gasoline had over benzene is questionable to-day.

ABSENCE OF OBJECTIONABLE ODOR, both in the fuel itself and in the exhaust products. The odor of motor benzene is certainly no more unpleasant that that of petrol or gasoline. The prevention of an offensive exhaust depends on the completeness of combustion, and the sulfur content of the fuel.

NO LIABILITY TO FORM DEPOSITS in the cylinders and valve passages. The author's experience tested a so-called *good* gasoline for residue and found 0.075 per cent compared to 0.027 per cent for motor benzene.

ECONOMICAL CONSUMPTION—Here is the point of most importance to the average motorist. All the above qualities must be met by any manufacturer or distributor in the form of good will or reputation, but the big question—How much will it save the public? How much will it save me? Benzene here has a decided advantage, as one would expect from a consideration of the relative calorific values:

CALORIFIC VALUE OF MOTOR FUELS (BRAME)

FUEL	Sp. Gr. 15.5° C.	CALORIFIC VALUE	
		B.t.u. per Lb.	B.t.u. per Gal.
Gasoline (Pre-war)	0.680–0.76	18,450	132,500
Benzene (90's)	0.883	17,100	150,000

"The motorist thinks of fuel in terms of gallons, not of pounds, and from his point of view the calorific value of benzene is approximately 13 per cent higher than that of petrol or gasoline. When benzene is used in an engine not only is more power available, but the thermal efficiency of the engine is usually found to have increased." The practical standard is mileage per gallon, and, given a suitable mixture, benzene is far superior to petrol in this respect. The high mileage figures obtained by the Automobile Association and the Royal Automobile Club are evidence of this, and may be supplemented by a number of authoritative trials, the results of which have been published during the past ten years. The average of such tests made by different observers on different types of cars, gives an increase of 22.7 per cent in miles per gallon. These tests were all taken without alteration to the compression ratio of the engine; but owing to the temperature of spontaneous ignition of benzene being higher than that of petrol, the compression, which is usually 70 to 75 lbs. per sq. in. in a petrol engine, may safely be increased to 150 lbs. in the case of benzene—with obvious further economy.

"The rate of propagation of the flame when using benzene is less than that in a petrol-air mixture. There is, in consequence, a marked reduction of any tendency to 'knock' under heavy loads, and ignition may be advanced to a greater extent with a view to eliminating this knock and its serious effects on the engine."

The reason why more mileage can be obtained from a gallon of motor benzene than from straight gasoline is that benzene permits the use of a leaner mixture. All aromatic compounds contain a higher percentage of carbon than the corresponding saturated hydrocarbon so that more air can and should be used in burning them.

In some cars carbon forms more readily; therefore, more heat is produced. If proper care is exercised to make sure the fuel has sufficient air to burn it, very little carbon will form. This is true of all motor fuels, particularly motor benzene. Remember your engines are not supposed to run perpetually without going over them. See if your carburetor is adjusted properly before you condemn a fuel. Benzene has not only been proved to be the best fuel fos an internal combustion engine by all scientific men of the world, but it actually demonstrates the fact.

A Request for Journals

The "American Medical Aid for Russia," with headquarters at 103 Park Ave., New York City, desires to secure three copies of important scientific publications issued in this country since 1914. They are intended for use at the University of Petrograd, University of Moscow, and Moscow Academy of Sciences.

Anyone who is willing to contribute copies of the SOCIETY'S journals from 1914 to the present date should communicate with the organization at the above address.

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[1] Received March 6, 1922.

Recovery of Platinum from Used Contact Mass at the Old Hickory Powder Plant[1,2]

By A. L. Kibler

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IN July 1920 there appeared an interesting account[3] of the scientific detective methods which were employed in bringing to light the theft of approximately 2300 oz. of platinum from the War Department. It will be remembered that the stolen platinum represented the platinum which was present at the Old Hickory Plant at the time of the Armistice in the form of platinic chloride solution from which the metal had been recovered by a simple evaporation to dryness and an ignition, either in the form of platinic chloride or ammonium chloroplatinate. It is perhaps not so generally known that this platinum constituted only a comparatively small part of the total platinum accumulated by the War Department, by far the larger part of which was in the form of contact mass designed for use in the manufacture of sulfuric acid. An account of the recovery of the valuable metal from the immense quantities of contact mass which the cessation of the war left in the hands of the War Department would appear to be of interest to the chemical world.

The Old Hickory Powder Plant, the world's largest smokeless powder plant, was designed to manufacture a million pounds of smokeless powder a day, starting from the ultimate raw materials —raw cotton, sodium nitrate, sulfur, alcohol, and benzene. In addition to the powder plant, as such, there were therefore plants for the purification of raw cotton, and for the manufacture of nitric acid, sulfuric acid, ether, and diphenylamine. Each of these plants was laid out on a vast scale. The sulfuric acid, with which we are particularly concerned in connection with the subject of this article, was supplied by thirty complete sulfuric acid plants of the largest proportions, arranged in the form of fifteen twin sulfuric acid lines. For each plant there were four "converters" for the catalytic oxidation of sulfur dioxide to sulfur trioxide, each converter containing approximately 4000 lbs. of contact mass, arranged on five circular screens or shelves of heavy iron wire. The two lower screens held contact mass of 0.15 per cent platinum content; the next two screens held contact mass containing 0.20 per cent of platinum, while the upper screen held contact mass containing 0.30 per cent of platinum. Each sulfuric acid plant contained, therefore, approximately 16,000 lbs. of contact mass containing approximately 32 avoirdupois pounds of platinum or 466.5 troy ounces. The thirty plants would therefore contain approximately 14,000 oz. of platinum. Five of these plants, however, had not been supplied with contact mass at the time of the Armistice. The platinum for the manufacture of the contact mass for these plants was on the premises in the form of platinic chloride and it was the platinum from this material—or the larger part of it—the theft of which was reported in the article above referred to.

In addition to the 400,885 lbs. of contact mass contained in the sulfuric acid plants at the Old Hickory Powder Plant, 112,941 lbs. of contact mass were also in use in the second great smokeless powder plant of the War Department, located at Nitro, W. Va. This mass was shipped to the Old Hickory Powder Plant to be worked up for the recovery of its platinum content along with the larger amount at the latter plant.

Historical

In October 1920, the writer of this article was requested by the Ordnance Department of the War Department to undertake the task of recovering the platinum from the entire amount of contact mass then located at the Old Hickory Powder Plant. At that time the opinion seems to have been general in the Ordnance Department that the platinum which was stolen had been recovered from contact mass and that an adequate plant for the recovery of platinum was in existence at the Old Hickory Powder Plant, and the writer was so informed. When he arrived at Jacksonville on November 1, 1920, however, he found that practically no preparation had been made for the work to be carried out and that the process proposed for use had been worked out only on a laboratory scale by a method which was practically an analytical laboratory method.

The contact mass at the Old Hickory Powder Plant, like that used in the majority of contact process sulfuric acid plants in the United States during recent years, was prepared by spraying fused, grained magnesium sulfate with a solution of platinic chloride and roasting this sprayed mass to reduce the platinum salt to metallic platinum. Such contact mass, as well as all contact mass in which a stable soluble salt is used as the carrier, is covered by the Schroeder patent.[4] Among other advantages claimed for such contact material is the ease of recovery of the platinum which is expressed in the following language:

> Inasmuch as the furnace gases, even after purifying, still contain traces of dust, the contact bodies in the course of time become covered with thick impenetrable layers, which diminish their efficiency. To lay bare the surface, it is only then necessary to stir the contact body in water and to evaporate the salt solution thus formed. The dust is thereby dispersed throughout the entire mass and can no longer diminish the penetrability of the surface. Finally the dust may be readily separated from the platinum after dissolving out the salts which serve as the vehicle. For this purpose it is only necessary to boil with concentrated muriatic acid the slime which has been separated from the salt solution, whereupon the particles of dust pass into solution while the platinum black remains behind in a pure condition.

That the recovery of platinum from contact mass is not as simple as would appear from the above quotation is a matter of common knowledge among sulfuric acid manufacturers and platinum dealers.

In developing the process which is here described two sets of mutually opposed factors operated to restrict the logical and orderly development of an economical and efficient recovery plant. These factors were:

1—The recovery plant was to be a temporary affair, to be scrapped at the completion of the work for which it was designed. For this reason the purchase of expensive apparatus was prohibited except in case of absolute necessity, and the use of makeshift appliances from stock already in the possession of the Government and on the ground at the Old Hickory Powder Plant was encouraged.

2—It was discovered, after the construction of the recovery plant was almost completed and the equipment purchased, that the funds from which the work was to be done would expire on June 30, 1920, and that all activity must cease on that date. Plans had been submitted and equipment purchased on the basis of the turnover of 15,000 lbs. of contact mass per week, at which

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[1] Received April 7, 1922.

[2] Published by permission of the Chief of Ordnance.

[3] *Chem. Met. Eng.*, **23** (1920), 93; This Journal, **12** (1920), 815.

[4] U. S. P. 636,925, November 14, 1899.

rate the complete recovery could not be completed until October of that year. In order to meet this emergency the proposed output of the plant had to be more than doubled and the recovery plant had to be operated continuously with three working shifts.

During the actual operation of the plant the main object, therefore, was to recover the bulk of the platinum in a condition suitable for storage before June 30, 1920, and a high percentage of recovery, the purity of the recovered platinum and accurate current control of the recovery process were all subordinated to this object.

ACCOMPLISHMENTS

Of the 513,826 lbs. of contact mass on hand at the Old Hickory Powder Plant, 133,830 lbs. were shipped away as such to be stored or otherwise disposed of by the Government. In addition to this, 36,755 lbs. of unroasted mass, containing all its platinum in soluble form, were withdrawn for other purposes. These withdrawals left 343,241 lbs. to be worked for platinum recovery. The amount of platinum which this should contain is shown in Table I.

TABLE I

	Mass Lbs.	Supposed Pt Content Per cent	Pt Content Troy Oz.
	156330	0.15	3418.9
	124684	0.20	3635.8
	62227	0.30	2721.8
	343241		9776.5
Deductions for samples	400	Av. 0.20	12
NET	342841		9764.5

These figures are based on the amount of platinum which was supposed actually to have been sprayed on the magnesium sulfate in the manufacture of contact mass, calculated to give the platinum percentages shown. There were, however, unavoidable losses of platinum between the time that the platinum solution was sprayed and the time that the contact mass was delivered to the recovery plant to be worked for platinum. The operations involving loss are the following:

1—When the solution of platinic chloride was sprayed on the granulated magnesium sulfate.

2—When the sprayed mass was roasted.

3—When the roasted mass was transferred to the converters.

4—During the operation of the converters.

5—During the unloading of the converters and the transfer of the mass to the recovery plant.

It should also be noted that the above tabulation assumes a normal platinum content in the entire weight of contact mass as delivered to the recovery plant. This would include the not inconsiderable amount of sand, iron rust, and other impurities which the mass picked up during its handling and use.

It is believed that the discrepancies caused by the above-named factors would amount to from 5 to 10 per cent of the platinum content shown in the above tabulation, and that 7.5 per cent is a conservative figure to use as a basis of calculation. Deducting 7.5 per cent of 9764.5 oz., we have 9032 oz. as the actual amount of platinum to be recovered.

There were actually recovered 8812 troy oz. of platinum sponge. The exact purity of this sponge is not known. The several lots varied considerably in purity, and there were also variations in the several parts of the same lot. Accurate analyses would have necessitated very thorough blending of large amounts of platinum sponge which would have involved considerable loss of platinum and more time than was available. Moreover, as has been pointed out above, the Ordnance Department was not so much concerned with the purity of the recovered platinum or with an accurate control of the process as it was in the completion of work within the limited time. Some analyses were made on imperfectly blended samples and these analyses indicated a purity of about 94 per cent. On this basis the platinum sponge recovered contained 8283 troy oz. of actual platinum. On the basis of these calculations a recovery of 91.7 per cent has been achieved. Of the remaining 8.3 per cent or 749 troy oz., 400 to 500 troy oz. of recoverable platinum have been accounted for in the residues left from the plant operations, the working of which was impossible within the limited time. Adding 450 oz. to the 8283 oz. recovered, we have 8733 oz., or a 96.7 per cent recovery.

CONSTRUCTION AND INSTALLATION OF PLANT

Active work on the construction of the platinum recovery plant was begun during the last week of December 1920. The building, which was designated for the recovery work prior to November 1, 1920, was one of the poacher houses previously used for the purification of nitrocellulose. This building was about 75 ft. wide and 290 ft. long. The equipment previously used in it for purifying nitrocellulose consisted of four rows of large wooden tubs approximately 13 ft. in diameter and 11 ft. deep, together with machinery for agitating the contents of the tubs. The tubs were built on foundations consisting of parallel walls of brick covered with concrete, approximately 2 ft. high and 1 ft. thick. Previous to the arrival of the writer at Old Hickory three of these tubs in one row at one end of the building had been elevated to a height about 4 ft. above their old foundations, the three opposite tubs in the next row had been torn down and the parallel walls which served as their foundations had been closed at the ends, thus making three rectangular concrete-lined tanks, measuring approximately 13 ft. by 7 ft. by 2 ft. deep. It was decided to use this end of the building for the recovery plant and the opposite end for storage of materials and supplies. This left about 105 ft. in the center of the building which could not be used.

The construction of the plant and the installation of machinery were practically completed by the first of March 1921. The principal items of construction and installation are listed below:

1—Alteration of small building for use as a laboratory and office, and installation of laboratory equipment.

2—Partition across poacher house to enclose the portion to be used in the recovery process.

3—Installation of 40 h. p. locomotive type steam boiler with complete system of steam pipes, radiators for heating entire plant and for use in the process.

4—Installation of lighting and power service wires for laboratory and plant.

5—Installation of telpherage system with 350 ft. of 30-in. tram track, with two inclines, for delivering contact mass, acid, etc., from the storage room to the solution tubs and other points in the recovery plant.

6—Installation of 30 h. p. motor for tub agitators, 10 h. p. motor for telpherage system, other motors for air compressors, three centrifugal pumps, centrifuges, and exhaust fans.

7—Installation of water pipes and connections.

8—Construction of two heating tables 30 ft. by 5 ft., heated by oil burners, one at each end. Each table was constructed of fire brick and fire clay slabs and contained a layer of about 3 in. of sand on the heating surface. Above each table and enclosing it a large fume hood and exhaust flume were constructed, the exhaust fan being placed so that the fumes were siphoned out of the hood and did not pass through the fan. Sliding doors on each side gave access to the heating surface of the table.

9—Construction of a roasting oven for final stage of platinum purification. The heating chamber was constructed of fire clay slabs and measured 7.5 ft. by 2.5 ft. by 16 in. high. It was heated by an oil burner and was so built that the gases from the combustion of the oil could not enter the heating chamber but circulated around three sides of it.

10—Installation of four Sharples supercentrifuges and one centrifugal laundry wringer.

11—Installation of laundry dryer.

12—Construction of vault for platinum storage.

13—Installation of three 30-gal. earthenware jars, three 75-gal. earthenware jars, and twelve 264-gal. earthenware jugs, with connections.

14—Wire fence around entire plant.

15—Repair of concrete-lined save-all tank 50 ft. by 100 ft. by 6 to 7 ft. deep for storage of spent aqueous liquors.

Construction had advanced sufficiently by the middle of February 1921 for operations to begin on an experimental scale, and active and continual operation was begun about the first of March.

Outline of Process

The process as finally worked out was as follows:

1—Solution of the water-soluble portions of the contact mass in hot water.

2—Allowing the charge to settle.

3—Separation of insoluble portions by means of the Sharples supercentrifuge.

4—Concentration of the platinum sludge by means of weak hydrochloric acid.

5—Separation of concentrated platinum sludge from the weak acid wash by means of the Sharples supercentrifuge.

6—Digestion of the "concentrated sludge" in aqua regia, evaporation of aqua regia to dryness, addition of two separate portions of hydrochloric acid followed after each addition by evaporation to dryness, extraction of the platinic chloride formed by means of two to three treatments of dilute hydrochloric acid, the solution being siphoned off after each treatment, the whole procedure repeated two or three times.

7—Precipitation of platinum as the ammonium chloroplatinate by the addition of ammonium chloride to the hydrochloric acid extract.

8—Washing the ammonium chloroplatinate several times with alcohol, separation of the wash liquors being effected by allowing to settle and siphoning off through glass siphons.

9—Final separation of the ammonium chloroplatinate from the alcoholic wash liquors by means of a centrifugal laundry wringer.

10—Drying the ammonium chloroplatinate in a laundry dryer.

11—Roasting the ammonium chloroplatinate to platinum sponge.

12—Recovery of platinum from the waste acid and alcohol liquors by precipitation with zinc solution in aqua regia and subsequent purification as above described.

Details of Process

DESCRIPTION OF CONTACT MASS—The contact mass as unloaded from the converters was usually of a light gray color and granular form, the size of the granules being approximately such as would pass through a 0.5-in. mesh screen. In the converters which had been in use for the longest time the granules had frequently coalesced into large soft lumps containing a considerable quantity of sulfuric acid. This was particularly noticeable in the mass from the top screens in the converters and was probably due to a condensation of sulfuric acid on the mass. The mass also contained considerable quantities of iron rust from the interior of the converters and the screens. Some of the iron rust was in the form of very fine dust and was probably carried over mechanically by the current of sulfur dioxide from the other apparatus through which it had passed. This iron was particularly troublesome in the process, being very difficult to separate from the platinum. It was also very troublesome in analytical work since it was particularly difficult to get into solution, some of it not going into solution even on long boiling in aqua regia. Fusion with sodium carbonate proved the best way to get this particularly insoluble form of iron oxide into solution for analytical work. There was also a considerable quantity of granular magnesium hydroxide or oxide in the mass. This was probably formed by roasting the mass to so high a temperature as to break down the magnesium sulfate. In one case nearly two barrels of these coarse granules were shoveled out of a solution tub after the treatment of a 15,000-lb. charge of contact mass. The solutions of such charges were, of course, alkaline in character.

The impurity present in the largest proportion was ordinary sand. This may have come from the tops of the preheaters which were covered with a layer of several inches of sand for insulation and were located very close to the converters. The sand could have blown into the converters while they were being filled or it could have been carried in by careless workmen. There was also present a considerable quantity of soluble silicates which formed silicic acid gel when in the presence of acid liquors and caused great difficulty at various steps in the operation. It was impossible to filter any of the acid solutions on account of this silicic acid.

SOLUTION OF CONTACT MASS—Solution of the water-soluble portions of the mass was carried out in large wooden tubs which were originally designed as poacher tubs in the purification of pyrocellulose for smokeless powder. They measured approximately 13 ft. in diameter and approximately 11 ft. deep. One foot in depth held approximately 1000 gal. of water. A normal charge for these tubs was 15,000 lbs. of contact mass and 6000 gal. of water. The optimum conditions for charging this amount were as follows: 6000 gal. of water were run into the tub and heated with steam to 65° to 70° C. The contact mass was then fed into the tub at such a rate as to require 7 to 8 hrs. for the addition of 15,000 lbs., the temperature during the addition not being allowed to exceed 90° C. The agitators were kept running throughout the time of charging and for 3 hrs. thereafter at the constant speed of about 15 r. p. m. The agitators were then stopped and the charge allowed to stand from 24 to 36 hrs. Occasionally the charge settled sufficiently to allow several feet in depth of the liquid to be siphoned off from the top of the charge. More often, however, a sufficient amount of solid matter was held in suspension to necessitate the centrifuging of the entire charge. When this was the case centrifuging was started from the 0.75-in. outlets with which the tub was provided at distances of about 1 ft. apart, beginning with the opening nearest the top of the liquid. In this way the charge was drawn off through the centrifuges without agitating the charge until there were about 1.5 to 2 ft. of charge in the tub. At this depth a considerable amount of sludgy material began to be collected in the centrifuges, and it was very difficult to make a clean separation between the solid and the liquid on account of the large amount of solid and the high specific gravity of the liquid. At this point the charge was usually diluted with water to about twice its volume. The agitators were started and run for a few minutes until the charge was thoroughly mixed. It was then allowed to settle from 0.5 to 1 hr., and again centrifuged, starting from the top openings as before. A much better separation was then secured on account of the lowering of the specific gravity of the solution. When large amounts of solids again began to collect in the centrifuge bowls, a second dilution was given and sometimes a third and a fourth, depending on the nature of the charge. The sludge obtained after such dilutions was almost free from magnesium sulfate.

The centrifuge bowl in which the sludge was collected was a monel-metal cylinder, approximately 30 in. long and 4.5 in. outside diameter, with 0.5-in. wall. It revolved at a speed of 16,000 r. p. m.

The liquid to be centrifuged passed into the bowl through a central hole at the bottom, the solids in the liquid adhered to the walls of the revolving bowl by centrifugal force, and the clear liquid passed out of the bowl at the top. When approximately 10 lbs. of solid material had been collected the centrifuge was stopped, and the bowl was taken out and emptied into pans. The sludgy material thus obtained contained practically all the platinum from the original mass and a large quantity of other materials, chiefly iron rust, insoluble magnesium salts, sand, and gelatinous silicic acid.

The effluent from the centrifuges was usually quite clear. It was first run into the rectangular sump tanks previously described. When a sump tank was full it was tested for dissolved platinum. If there was no appreciable amount of platinum in solution and if the liquor was clear it was pumped out and run into a large concrete-lined save-all tank for storage. If it contained dissolved platinum it was heated with steam, and hydrochloric acid and zinc were added to precipitate the platinum. After cooling it was again run through the centrifuge. If the liquor was not clear it was centrifuged again before running to the save-all tank.

The contact mass which has been in actual use in converters was usually slightly acid to methyl orange after being dissolved in water. Occasionally a charge was found which was slightly alkaline. This was the case with many of the charges of the Nitro mass. This alkalinity was due to the presence of magnesium hydroxide which might have been formed by an overheating of the mass. At times magnesium hydroxide was present in very large quantities, so large as to make it impracticable to dissolve it with acid. In one case after the addition of 250 gal. of commercial hydrochloric acid the charge was still alkaline and, as stated above, 2 bbls. of coarse magnesium hydroxide mixed with sand were shoveled out of the bottom of the tub after the charge was run out.

Charges which were alkaline settled better than acid charges but usually yielded a very much larger quantity of sludge than the acid charges. On one occasion two charges which were strongly acid in reaction were neutralized with milk of lime to facilitate settling. The charges then settled rapidly and about 3 ft. of clear water were siphoned off from the top of the charge. An immense amount of voluminous, slimy sludge, however, was found at the bottom of these charges. In one case there were almost a thousand pounds of this sludge and it contained calcium salts which gave very great difficulty throughout all the remaining processes and even showed up in the platinum sponge. The best practice consisted in centrifuging the charges just as they were without the addition of either acid or alkali. When charges were alkaline the amount of granular magnesium hydroxide was usually so large as to make it impracticable to dissolve it by the addition of acid and, moreover, the addition of acid caused appreciable amounts of platinum to go into solution in the liquor. If the charge was acid the addition of alkali caused the precipitation of large quantities of iron, magnesium salts, and other compounds.

It was sometimes found that 15,000 lbs. of contact mass were too much for 6000 gal. of water, and in this case the charge was cut down accordingly. This was especially the case with contact mass which had been in use for some time. In the case of mass from the first converters which were put into operation at the Old Hickory Powder Plant, the charge of mass for 6000 gal. of water was reduced to 10,000 lbs. These charges were strongly acid with sulfuric acid and contained large lumps of material which had apparently been formed by the condensation of sulfuric acid within the converters. With these charges it was found impossible to obtain a complete separation of the liquid and solid with the centrifuges unless the concentration of the solution was lowered by the addition of more water.

In all cases when the charge had been run out through the centrifuges to within 6 to 10 in. of the bottom, the remainder of the charge was run out through a 4-in. opening in the bottom of the tub into the concrete-lined sump tank opposite the tub, being passed through a coarse mesh copper screen to catch large sized gravel and other foreign material which the contact mass contained. From the sump tanks it was pumped to a series of bath tubs which were located over the centrifuges at a sufficient height to give head enough to run well through the centrifuges. The material which collected on the screen was washed thoroughly with water until the water coming through the screen was clear. The material then remaining on the screen was collected in barrels and designated "sandy residues."

There was a very wide variation in the amount of sludge obtained from the several charges. Some charges yielded less than 100 lbs. of sludge, while others yielded nearly 1000 lbs. The two charges to which milk of lime was added, as previously referred to, yielded very voluminous sludges containing large quantities of insoluble calcium salts, iron hydroxide, magnesium hydroxide, sand, etc. Of the charges not so treated the variations in weight were usually due to magnesium oxide or hydroxide, iron oxide, and sand.

The average amount of time required to clean up a charge completely after the centrifuging began was 56 hrs., four centrifuges being used, and centrifuging being carried on 24 hrs. per day, 7 days per week.

WEAK ACID CONCENTRATION—It was discovered that the sludge obtained from the several charges could be very materially reduced in bulk and weight by a weak hydrochloric acid treatment, with an acid sufficiently weak to pass through the centrifuges without very rapidly attacking the centrifuge parts. The total amount of sludge obtained from the twenty-five charges of contact mass was over 5000 lbs. This was reduced to 2000 lbs. by the weak acid treatment.

The weak acid treatment was carried out in a battery of stoneware jars consisting of two 75-gal. jars and three 30-gal. jars, all of which could be emptied through faucets into a 10-gal. crock from which the centrifuge was fed. The jars were filled with a charge in a ratio of 12.5 lbs. of sludge to 1 gal. of hydrochloric acid (31 per cent HCl), and 4 gal. of hot water. The sludge was put in the jars, and the acid was added and stirred up for several minutes with a wooden paddle. The hot water was then added and the whole again stirred. It was then allowed to stand from 18 to 24 hrs., or until cool enough to centrifuge. Occasionally, if a sludge was quite alkaline in character, it was necessary to add an additional amount of acid and water in order to make it centrifuge properly. Approximately 500 lbs. of sludge could be charged into the battery of jars at one time, although this was usually more than the one centrifuge which was allotted to this work could handle in one day's time.

PURIFICATION. *Aqua Regia Treatment*—In principle the purification stage consisted of an aqua regia treatment of the concentrated sludge in order to carry the platinum into solution, a complete evaporation of the aqua regia solution in order to eliminate the nitric acid, solution of the platinum chloride in hydrochloric acid, separation of the hydrochloric acid solution of platinum from the residual solid matter, precipitation of the platinum in the form of ammonium chloroplatinate by the addition of ammonium chloride, separation and washing of the ammonium chloroplatinate, drying of the ammonium chloroplatinate, and roasting it to sponge.

Approximately 5 lbs. of concentrated sludge in a large silica dish (about 6-gal. capacity) were placed on the hot table. About 10 qts. of commercial hydrochloric acid were then added. This was thoroughly heated and mixed by means of wooden paddles. About 3 pints of nitric acid were then added very carefully, a little at a time, to avoid violent frothing. In the beginning the amount of nitric acid to be added at a time should be not more than 25 cc. or even less. Nitric acid should be added until a further addition causes no bubbling or frothing. One part of nitric acid to three parts of hydrochloric acid was usually sufficient.

The contents of the dish were then allowed to evaporate just to dryness. The residue could not be allowed to become caked since this was likely to break the dish. A small amount of hydrochloric acid was then added in such a way as to moisten the entire residue and this was again evaporated to dryness. About 3 qts. of hydrochloric acid and 5 qts. of water were then added to the contents of the dish and digested until the residue was loose from the dish and thoroughly disintegrated. The disintegration can be assisted by the use of wooden paddles. The entire contents of the dish were then poured into a 10-gal. crock, the dish being washed out with just sufficient water to transfer the contents. Several dishes were emptied into one 10-gal. crock until the crock was almost entirely full. The crocks were then allowed to stand for 24 hrs. or longer, until complete settling had occurred and the supernatant liquid was clear. The clear liquid was carefully siphoned off into 10-gal. crocks by the use of 0.25-in. glass siphons, the crocks being tilted gently so that the clear liquid might be siphoned as completely as possible. The residue left in the crock after siphoning was treated with 1 part hydrochloric acid and 2 parts hot water, with stirring, so that the solid residue was thoroughly mixed with the hot dilute acid. This was again allowed to cool and settle and the clear liquid also siphoned off and added to the liquid previously siphoned. The residue which was now in the crock was returned to the silica dishes and the entire process just described was repeated, using the aqua regia treatment and two weak hydrochloric acid extractions. The residue then usually contained from 0.2 to 0.4 per cent of platinum and was set aside in containers for final disposal by the Government. Occasionally, however, a third and even a fourth aqua regia treatment was necessary.

The process above described was adopted because filtration of the strongly acid, hot solutions was found to be particularly difficult and very slow. The objections to the siphoning process are, first, that it leaves a small amount of impurities in the finished platinum sponge, and, second, it is not possible to strip the residues quite as free from platinum as could be done with a suction filter.

Precipitation—The clear liquors which had been siphoned off after the several hydrochloric acid extractions were treated with a hot concentrated solution of ammonium chloride in order to precipitate the platinum as ammonium chloroplatinate—a highly colored yellow salt. Hot solutions of ammonium chloride were used because a much larger amount of ammonium chloride per unit of volume could be added, thus obtaining the most insoluble medium for the ammonium chloroplatinate. For the same reason, the first portion of ammonium chloride was sometimes added in solid, finely powdered condition. After the precipitation, about 2 per cent of 95 per cent alcohol was added in order to facilitate the settling of the ammonium chloroplatinate. If any oil was present, which was usually the case and which came from the centrifuges, a considerable amount of yellow salt might float in a scum on the surface. This scum was made to sink by the addition of a few drops of ether and gentle agitation of the surface. Unless the nitric acid had been completely removed by evaporation of the aqua regia in the preceding stage, violent frothing was likely to occur on the addition of alcohol, either at this stage or the following stages where the precipitate was washed with alcohol. This frothing was sometimes so violent as to cause the loss of practically the entire contents of the crock if precautions were not taken.

The crocks were allowed to stand undisturbed for 12 hrs. after precipitation. At the end of this time the clear supernatant liquid, which had previously been tested in order to determine whether precipitation had been complete, was carefully siphoned off through glass siphons as completely as was possible without drawing over some of the yellow salt. The yellow salt from several crocks was usually concentrated into one crock at this stage and the crock filled up with alcohol. This was again allowed to stand for 24 hrs., or until settling was complete. The supernatant liquid was siphoned off as before and a second alcohol wash was given. It was found advantageous to repeat this alcohol wash three times. All liquids siphoned off from the yellow salt were stored in 26½-gal. earthenware jugs, a supply of which was available on the plant. These were afterwards treated for the recovery of the dissolved platinum as will be described later. The alcohol used in this process was colored with methylene blue to discourage its use as a beverage.

Separation of the Ammonium Chloroplatinate from the Wash Liquor—After the third alcohol wash the yellow salt, in the form of a thick sludge, was transferred to a 75-gal. jar which was located on an elevated platform over an ordinary centrifugal laundry wringer. The revolving basket of the wringer was approximately 10.5 in. deep and 26 in. in diameter and revolved at about 1150 r. p. m. The sides, perforated with about 0.25-in. holes, were lined with a very heavy woolen filter cloth.

The sludge in the 75-gal. jar was diluted with alcohol to the consistency of thin cream and fed through a rubber hose, with constant stirring, into the center of the revolving wringer bowl. The rate of feeding had to be very carefully controlled by means of an earthenware stopcock and could be learned only by experience. A slight over-balancing of the bowl by the collection of too much material on one side would cause such violent vibration that the wringer might have to be stopped and the charge dipped out and returned to the storage jar. When properly fed the alcohol passed through the woolen filter cloth, leaving the yellow salt in the form of a comparatively dry cake, packed against the walls of the bowl. By careful feeding as much as 40 lbs. of yellow salt were collected in one charge. The average weight of the charge was about 25 lbs. It was removed from the wringer by scraping down from the sides with a large spoon and scooping it into enameled dish pans, in which it was dried.

The yellow salt as it came from the wringer contained about 18 per cent volatiles, mostly alcohol. It was dried by placing the pans containing the wet salt on racks in a laundry dryer. This dryer consisted of a galvanized iron box, 6.5 ft. by 8 ft. by 8 ft. high, lined on three sides with double coils of steam pipe. It heated in a very short time and attained a temperature of 95° to 100° C. The yellow salt was sufficiently dried if left in the dryer over night.

Roasting of Yellow Salt—For the roasting of the yellow salt, 36-qt. graphite crucibles with tops and lined with zirconia were provided. These crucibles were sufficient to handle the amount of yellow salt which was originally designed to be roasted at one time. With the speeding up of the process, however, they were entirely insufficient, and time did not allow the purchase of an additional supply, since they were not carried in stock. Two very large graphite crucibles, such as are used in brass foundry works, were found in the shop area of the powder plant. They held approximately 1.5 gal. each, but were still not sufficient to hold the large amounts of yellow salt which had to be roasted at a time. The large silica dishes which were in use in the aqua regia treatment of the sludge proved entirely satisfactory for the roasting process, except that they were awkward in shape and were so large that they could not be provided with covers. In the larger roasts two of these silica dishes were used and filled with yellow salt to within 4 in. from the top. By the use of all these expedients and by carefully arranging the vessels in the roasting ovens, an amount of yellow salt sufficient to yield 1000 oz. of platinum sponge was roasted at one time. The muffle furnace which was used for roasting was constructed in such a way that the combustion gases could not pass through the heating chamber but circulated completely around it. It was heated by means of an oil burner with a steam jet.

The following is a description of a typical furnace run: The several crucibles and silica dishes containing the yellow salt were carefully placed in the furnace in such a position that they could be withdrawn with tongs while the furnace was still hot. The temperature of the furnace, while being charged, was usually 400° or 500° F. The door was then closed and sealed. The oil burner was lighted and kept going for approximately 24 hrs., during which time the temperature rose to approximately 1300° F. Dense white and yellow fumes began to appear when the temperature of the furnace reached approximately 500° F. These continued for 12 to 15 hrs. By the time the temperature had reached 1300° F. the fumes had practically ceased. The burner was kept on for about 2 hrs. after the fumes ceased to issue from the furnace. The fire was then shut off and the furnace allowed to cool to a temperature at which it could be opened and the crucibles taken out.

The yield of platinum sponge from the dried yellow salt usually ran a little over 100 per cent of theory, owing to the presence of impurities. These impurities were chiefly silica with a little iron. The lowest yield obtained was 93.7 per cent of theory, in a case where the yellow salt was not completely dried. The highest yield obtained was 107.7 per cent of theory, the result of the fact that this roast was made up largely of platinum recovered from various residues and contained a larger amount than usual of impurities. The next highest yield was 103 per cent of theory.

Recovery of Platinum from Wastes—During the operation of the processes described in this report several waste products collected which contained considerable platinum. Those described below were treated to recover the platinum which they contained:

1—Oily drippings from the centrifuges.

2—Acid effluent from the centrifuges after the weak acid treatment of the sludge.

3—Acid liquors siphoned off from the precipitation crocks after the precipitation of ammonium chloroplatinate with ammonium chloride.

4—Weak alcohol wash liquors obtained by siphoning off from the crocks and effluent from the laundry wringer.

5—Rags which were used in cleaning the centrifuge bowls and other pieces of apparatus.

The treatments for the several waste products itemized above are enumerated consecutively below:

1—The oil and water were separated in vessels having a bottom faucet. When settling was complete the water was drawn off from below and run through the centrifuge to recover the suspended platinum. The oil was burned off in an open iron kettle and the residue treated with aqua regia on the hot table.

2—The weak acid water which contained approximately 15 oz. of platinum per 100 gal. was treated with zinc to precipitate the platinum. It was then run through the centrifuge to recover the precipitated platinum.

3—Same treatment as for (2).

4—Several 264-gal. jars of alcohol waste were distilled to recover the alcohol. The residue left after most of the alcohol was distilled off was precipitated with zinc and centrifuged. This process, however, proved too slow with the facilities which were available. It was found by laboratory tests that platinum could be precipitated practically completely in the presence of considerable alcohol if a large excess of zinc were used and a considerable time allowed for the reduction. The remaining alcohol liquors, were, therefore, precipitated directly with zinc and centrifuged.

5—The rags were burned in an open kettle and the ashes treated with aqua regia on the hot table.

All the platinum sludge obtained from the above-mentioned waste products was turned on to the hot table for purification with aqua regia treatment and worked up with the rest of the platinum sludge and was not kept separate. The amount of platinum recovered from these residues was probably in the neighborhood of 800 troy ounces.

Recoverable Platinum in Residues

It is very difficult to make an intelligent estimate of the platinum contained in the residues left in the Platinum Recovery Plant owing chiefly to the difficulty of obtaining average samples. Some analyses have been made of the various residues but it is believed that they can serve as an indication merely and not as the basis of an intelligent estimate. As nearly as can be ascertained the amounts of platinum in the various residues left in the Plant were the following:

1—The save-all tanks. These contained approximately 225,000 gal. of liquor which was nearly a concentrated solution of magnesium sulfate. It is estimated that there may be 100 oz. of platinum in solution in this liquor and 50 oz. in the form of fine sediment on the bottom.

2—Approximately 1000 lbs. of residue from the silica dishes, which should contain 100 oz. of platinum.

3—Approximately 1500 lbs. of sandy residues shoveled from the bottom of the solution tubs and washed. This should contain 100 oz. of platinum.

4—Approximately 500 lbs. of magnesium hydroxide shoveled from the bottom of some of the solution tubs. This should contain 25 oz. of platinum.

5—Approximately 200 gal. of wash liquor from the yellow salt. This should contain 30 oz. of platinum.

6—A clean-up of the solution tubs by knocking them down and scraping them and a clean-up of all the equipment used in the platinum plant should yield 50 oz. of platinum.

All these sources account for about 455 troy ounces.

Financial Statement

On November 1, 1920, there was an unobligated balance of approximately $23,561.66 of the allotment for the recovery of platinum. On March 1, 1921, there was an unobligated balance of approximately $8,367.84. The sum of $15,193.82 represents approximately the cost of the construction of the plant and the purchase of the initial apparatus. This sum includes the cost of four centrifuges for $6,800.00. Between March 1 and June 30, three additional allotments, totaling $18,500.00, were made. On June 30, the unobligated balance was approximately $1,840.74. The sum of $25,027.10, therefore, represents approximately the cost of operating the plant, although it includes some rather large items for maintenance and the purchase of supplies and additional equipment. The total amount of money expended between November 1, 1920, and June 30, 1921, was approximately $40,220.92. Figuring the actual amount of platinum recovered as 8283 troy ounces, the cost of recovery has been $4.855 per ounce. These figures do not take into account the value of the residues, from which the Government will probably realize an appreciable sum, and the value of the equipment which has been purchased and which remains the property of the Government.

Conclusion

Owing to the conditions under which the work here described was conducted no very extended laboratory work was carried out, though many problems of an unusually interesting nature presented themselves. However, some investigations of a pressing nature were conducted and some interesting results were obtained which, while not complete, may be made the subject of a separate article in the near future. In connection with the chemistry of platinum, reference might here be made to the excellent "Bibliography of the Metals of the Platinum Group" published as *Bulletin* **694** by the U. S. Geological Survey, and also to "The Detection and Estimation of Platinum in Ores," *Technical Paper* **270**, of the Bureau of Mines.

As this article goes to press the attention of the author has been directed to a review of "Technical Records of Explosives Supply 1915–1918, published by the Ministry of Munitions and Department of Scientific and Industrial Research, H. M. Stationery Office, London, 1921" in which the following statement appears: "Of special interest is **** the recovery of the magnesium sulfate and platinum, together with the separation of platinum and iridium, from contact mass." The publication reviewed is, unfortunately, not available to the author, and no comment can be made by way of comparison between the method therein described and that described in this article.

Acknowledgment

The writer desires to express his indebtedness to Dr. Charles E. Munroe of the National Research Council, Washington, D. C., for valuable suggestions in the compilation of this article and for his assistance in preparing it for publication.

First Report of the Committee on Contact Catalysis

By Wilder D. Bancroft

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(Concluded)

ADSORPTION BY METALS AND METALLIC OXIDES

At Princeton University Professor Taylor and his students have measured the adsorption of carbon monoxide, carbon dioxide, oxygen, hydrogen, and nitrogen at atmospheric pressure and different temperatures by various catalysts, such as copper oxide, manganese dioxide, cobaltic oxide, and silica (Benton), and of hydrogen, carbon monoxide, carbon dioxide, and ethylene, by finely divided nickel, cobalt, iron, copper, palladium, and platinum.[106] In the case of copper oxide the amount of adsorption has been shown to depend on the method of preparation, the adsorption being smaller the less active the material is catalytically. When the metallic oxides are prepared by precipitation processes, they show a high adsorptive capacity for carbon monoxide and carbon dioxide, while the adsorption of nitrogen and oxygen is small, and only a little hydrogen is taken up. The large adsorption of carbon monoxide and the small adsorption of hydrogen are significant in connection with the selective combustion of carbon monoxide in hydrogen. The general conclusions reached by Taylor and Burns[107] are quoted in full:

> From the experimental work here recorded we feel that certain important conclusions relative to the adsorption theory of contact catalysis have obtained decisive demonstration. Furthermore, we believe that the experiments are of importance in the general problem of adsorption, and disclose the operation of other factors, the significance of which, in reference to catalysis, needs special emphasis.
>
> Investigations of catalytic adsorbents of the type dealt with in these experiments show results which are in marked contrast to the results of adsorption measurements in which porous, chemically inert, materials such as charcoal and silica gel are used. In the case of metallic catalytic agents the adsorption is pronouncedly specific. In one of such cases hydrogen is more markedly adsorbed than other gases. For example, nickel adsorbs more hydrogen than carbon monoxide. On the other hand, the reverse is the case with iron and cobalt, these metals showing hydrogen adsorptions which are decidedly smaller than those of the other gases. The parallelism observed in the case of porous, inert adsorbents, such as charcoal, between adsorption, compressibility, and ease of liquefaction of the gas does not appear to hold in the case of adsorption by the metal catalysts which we have studied. The adsorption isotherms are also different, saturation capacity of the adsorbent being attained at rather low partial pressures of the gases.
>
> All of this evidence is in agreement with the view that adsorption in the case of metal catalysts is a surface phenomenon somewhat chemical in nature, possibly involving rearrangements of electrons on both the adsorbent and the gas. In the case of bodies like charcoal and silica gel, the phenomenon may be attributed frequently to the presence of pores which fill gradually with liquid, although covering of the surface by an adsorbed gas film can undoubtedly occur in this case also. At any rate, the experiments which have been performed demonstrate that the problem of adsorption by *solid* adsorbents is a far wider one than hitherto indicated, and that it promises to be more interesting by reason of the wide range of possibilities. A comprehensive scheme of study in this field has been planned and undertaken.
>
> The measurements with active nickel catalysts and with inactive nickel obtained by reduction of the oxide at elevated temperatures form, we believe, convincing experimental demonstration that the destruction of catalytic activity is accompanied by an almost complete suppression of adsorptive power. In addition, these results clearly indicate one reason for variability in catalytic behavior with variation in mode of catalyst preparation, a phenomenon widely known, but hitherto little understood. The varying adsorptive capacity of the material would account for such variable catalytic behavior. The results suggest, moreover, the necessity of obtaining, in the kinetic studies of catalytic action, the actual behavior of the catalytic agent as an adsorbent.
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> From an examination of our adsorption measurements, it is evident that maximum catalytic activity does not occur at temperatures at which maximum adsorption is shown. Indeed, in the case of copper, the hydrogenation of ethylene begins only at a temperature where the adsorption of ethylene is ceasing to be a measurable quantity. It is true that nickel begins to hydrogenate ethylene at ordinary temperatures, where adsorptions are very large, but it will be observed that at the optimum temperature for this reaction, 130° to 150°, the adsorption of ethylene is considerably less than that at the temperature at which reaction commences. Similar observations may be made with respect to a cobalt catalyst with carbon monoxide and hydrogen, and with nickel in the case of carbon dioxide and hydrogen.
>
> We regard this evidence concerning diminishing adsorption and increasing catalytic activity with temperature as demonstrating the necessity, in many catalytic reactions, of a free evaporation of both reactants and resultants from the catalyst surface. A strong or reversible adsorption of any of the participants in a reaction undoubtedly tends to render the catalyst surface inactive. At the same time it is possible that such an irreversible adsorption may, in certain cases, lead to a reaction between gases which only occurs with difficulty in the gas phase. Our experiments with palladium and platinum with carbon dioxide and hydrogen may be cited in illustration. The experimental data show that carbon monoxide is tenaciously adsorbed by both metals, and that at moderate partial pressures the gas probably covers the metal surface. In such case, hydrogen, in presence of carbon monoxide, can be adsorbed only on a surface of carbon monoxide and not on the metal. The union of carbon monoxide with palladium to form a Pd-CO surface complex is apparently such that at ordinary temperatures the reactivity of the carbon is enhanced, and with hydrogen, methanation results. With platinum, on the other hand, no reaction occurs at any temperature and the Pt-CO surface complex remains undecomposed. The evidence cited by von Hemptinne[108] as to the behavior of Pd-CO surface complexes at low temperatures (−20° and lower) is quite parallel to that occurring with Pt-CO complexes at all temperatures within the range investigated. There is evidence that the production of sulfur trioxide in presence of platinum is caused by the interaction of a Pt-O surface complex with sulfur dioxide molecules. In this case the slight tendency of sulfur trioxide molecules to evaporate constitutes a complicating factor.
>
> When such strong or irreversible adsorptions are not present, when evaporation of the reacting gases is relatively rapid, the conclusion seems inevitable that the condensation process disturbs the electron field of one or the other, or both of the reacting gases, thus bringing them into a reactive condition. Subsequently, on evaporation, by readjustment of the electron field, the active molecules may either regain their normal state, or, on the other hand, may collide with other molecules bringing about reaction. That the adsorption effect is not singly the cause of reaction has been suggested in the preceding paragraphs. We are disposed, therefore, to consider reaction as the resultant of at least two factors, the adsorption factor and the temperature factor. There is evidence as to how these two factors operate. For example, it is known that ethylene and hydrogen can be caused to react by purely thermal means. The temperatures required are high, being in the region of 500°. With a nickel catalyst present reaction occurs from room temperatures upward, and strong adsorption of both gases is shown by nickel. With copper a temperature of 150° is required for incipient action, and adsorption by this metal is much less pronounced than in the case of nickel. Similar observations hold in respect to

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[106] Taylor and Burns, *J. Am. Chem. Soc.*, **43** (1921), 1273.

[107] *Ibid.*, **43** (1921), 1284.

[108] *Z. physik. Chem.*, **27** (1898), 429.

the conversion of carbon monoxide and hydrogen by means of nickel and cobalt, the temperature required in the case of cobalt, the less efficient adsorption agent, being some 90° higher than with nickel for similar rates of reaction.

It would, therefore, appear that the adsorptive capacity is an index of the temperature at which reaction can be induced. Where adsorption is strong we have, presumably, a more marked or more frequent displacement of the stable configuration of the molecule than with a weak adsorption. Consequently, a lower temperature will effect interaction. In such manner, it is possible to correlate, qualitatively at least, the present data on adsorption with the known catalytic activity of the metals in the reactions chosen for study. The importance of this conclusion is sufficient to warrant a detailed study of the same with a view to obtaining a quantitative relationship between the temperature factor and the adsorption factor. Such a study undoubtedly involves an analysis of catalytic action in its relation to radiation theories. An experimental investigation upon such lines is in progress.

Pease and Taylor have studied reducibility of copper oxide by hydrogen. The reaction is autocatalytic, copper apparently being the catalyst. The reaction starts very slowly and works up gradually to a maximum rate as reduction proceeds. Further addition of copper hastens the reaction considerably. Since copper is the catalytic agent and since copper oxide is the substance to be reduced, it is clear that on any theory of catalysis the reaction can take place rapidly only at the interface between copper and copper oxide. The presence of water vapor in the hydrogen interferes markedly with the formation of the original copper nuclei from which the reaction zone spreads; but it has little effect on the subsequent reaction at the interface between copper and copper oxide. The presence of oxygen in the hydrogen inhibits strongly the reaction at the interface but apparently does not affect the formation of the original copper nuclei. The effect of oxygen is thus exactly the opposite of water vapor.

OVERVOLTAGE

Rideal[109] has attempted to formulate the relation between overvoltage (or overpotential as he calls it) and the catalytic activity of the metals.

On the adsorption theory the following viewpoint may be advanced. At any surface when equilibrium is established between metal and the surrounding medium, the number of molecules striking and becoming adsorbed on the surface will be equal to the number evaporating, although the actual number liberated and adsorbed per second will vary with the nature of the metal. Under these conditions the free energy equation

$$E = \frac{RT}{F} \log \frac{P}{C_H}$$

will hold for all metals. On the passage of current, however, discharge of hydrogen occurs with the formation of atomic hydrogen adsorbed on the metal surface (presumably by a pair of electrons, or one valence bond). The affinity of an atom of hydrogen for another atom at room temperature is so large (*ca.* 80,000 cal. per g. mol.) that immediate combination between neighboring atom pairs occurs, resulting in the formation of molecular hydrogen, which, however, is still attached to the metal by each atom, a hydrogen molecule occupying two elementary spaces on the metal surface. For very small currents, in rapidly agitated electrolytes and with metals which do not hold the molecules very firmly it will be evident that the rate of removal of the gas away from the surface by evaporation may quite easily approach the rate of supply of the gas ions, and no overpotential will result. On the other hand, if a molecule of hydrogen has to be vaporized before two empty spaces are left on the metal surface for the gas ions, it is evident that actual work has to be done by the gas ions in vaporizing the molecular hydrogen. Overpotential is thus primarily a measure of the energy necessary to *desorb* hydrogen gas from a metal surface. Two factors, however, permit of relatively large currents being passed for only a slight overpotential; one is the normal evaporation into an unsaturated electrolyte, similar to the so-called diffusion current, and the other is the tendency to the formation of bubbles. The hydrogen molecules attached to the metal surface are not at rest but are performing highly damped oscillations, and if the adsorbing forces are not too strong molecules can coalesce to form small bubbles, especially around small points, which, as has already been pointed out, will affect the electrode potential.

We should therefore expect bubble size to be an important factor in the η value when the energy of adsorption per gram molecule is small, but for large values of the latent heat the molecules are less mobile and bubbles are not formed so easily, consequently bubble size should have but a small influence on the overpotential. Confirmation of this deduction was obtained from experiments on the influence of temperature on overpotential which are detailed later.

The desorption theory of overpotential is also supported from another point of view. Calculation from Bohr's theory[110] of the structure of the hydrogen molecule indicates that 2000 calories per gram molecule are required to remove an electron from one atom to the other in a hydrogen molecule, which, according to the theory alluded to above, is the critical energy increment of the activation of hydrogen gas in free space, being of course less than that necessary for the formation of atomic hydrogen, which requires another increment of energy. This critical energy increment can be equated to the electrical energy required to adsorb a gram-molecule of gas from an electrode surface, or,

$$\frac{96{,}540 \times 2}{4.2} \times \eta = 21{,}000, \text{ or } \eta = 0.455 \text{ volt}$$

It follows that metals having η values equal to or exceeding 0.455 volt, should, if used as catalysts in hydrogenation processes, show no activity since the energy necessary for desorption exceeds that necessary for the activation of hydrogen in the gaseous state in the absence of a catalytic material.

It may be noted in passing that electrolytic reduction with metals possessing η values > 0.455 volt should be able to effect the reduction of substances which are not amenable to the catalytic process, further that no metal can possess an overpotential exceeding the value for which the energy exceeds that necessary for the desorption of atomic hydrogen or

$$\frac{96{,}540 \times 2}{4.2} \times \eta = 80{,}000 \text{ or } \eta = 1.80 \text{ volts}$$

Metals having an η value less than 0.455 volt should show catalytic activity, since the adsorbed hydrogen will not be entirely immobilized; and the catalytic activity should increase with decreasing values in the overpotential. This can be seen from the following considerations:

Imagine a hydrogen molecule oscillating between two plane surfaces situated parallel and close to one another, one plane surface being perfectly reflecting, and the other adsorbent. Every time the molecule strikes the reflecting surface it will be returned to the adsorbent one. Here it will oscillate in the field of attraction until sufficient time elapses for it to acquire energy by impact from other molecules or by radiation sufficient to permit of oscillation outside the range of attraction and regain the other surface when it will be reflected *de novo*. The alteration of the energy content of one molecule with the time is analogous to the energy distribution among a number of molecules at any given instant according to Maxwell's distribution law. It is evident that if the energy required for desorption is large, or the value of η high, the rate of interchange will be small, and the converse for substances possesses a small desorption energy. There is consequently a greater opportunity for two molecules of different reacting species to become adsorbed in juxtaposition to one another and so react than in the former case. Further, the rate of desorption or evaporation of the products of the reaction, which frequently governs the reaction rate, will be more rapid if the latent heat is small.

The following figures indicate how closely the catalytic activity in hydrogenation processes is related to the overpotential:

Metals in Order of Decreasing Catalytic Activity (Sabatier)	Overpotential η Volts	
Nickel	0.03	−0.21
Cobalt	0.03	−0.01
Platinum	0.09	−0.01
Iron	0.08	
Copper	0.36	−0.03

Palladium (η=0.23 to 0.46 volt) has also a marked catalytic activity in certain hydrogen-ion processes, while Dewar has shown that silver (η=0.05 to 0.15 volt) occasionally exhibits extraordinary activity.

According to Sabatier, the following metals are inactive in catalytic hydrogenation processes.

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[109] *J. Am. Chem. Soc.*, **42** (1920), 94.

[110] *Phil. Mag.*, **26** (1913), 1, 476.

METAL	Overpotential η Volts
Tin	0.43 to 0.53
Lead	0 42 to 0 78
Mercury	0.35 to 0.64
Zinc	0.66 to 0.70

It will be noted that the figures given for the overpotentials fluctuate within somewhat wide limits; thus different samples of copper may give values within the ranges 0.03 and 0.36 volt. This fact is in perfect accord with our knowledge of the variation in catalytic activity of this metal. H. S. Taylor and the writer have shown that a sample of ordinary copper wire will only appreciably catalyze the combination of hydrogen and oxygen at a temperature of 350°, while "active" copper produced by alternate oxidation and reduction is operative at 70° to 90°. Bright platinum ($\eta = 0.09$ volt) is ineffective for the oxidation of ammonia to nitric oxide, gray platinum ($\eta = 0.06$ volt) is extremely active, while black platinum ($\eta = 0.01$ volt) is found to be much too active for this conversion, nitrogen being formed in relatively large quantities.

Experiment has shown that in the case of copper, also, there is a close relationship between catalytic activity and overpotential. It appears probable that these fluctuations in catalytic activity and overpotential in the same metal may be ascribed to the same cause, a difference in the surface structure of the metal. Under the microscope these differences are noted usually as a transition from a crystalline inactive variety to a powdery amorphous, occasionally microcrystalline active variety. The crystalline form may be converted into the active variety by a process of continued catalysis or by the continuous liberation of hydrogen at its surface. Metals deposited by a high current density are more active and possess a lower overpotential than those deposited under normal conditions, an indication that the elemental, cubic space lattice of the crystal is not so active as residues or fragments of the cubes from which one or more corners may be missing. In electrodeposition the metallic ions tend to build up on the active form, and the same holds true for colloidal materials undergoing cataphoretic deposition. This gives an explanation, already proposed by Bancroft, for the formation of good deposits by such addition agents, and readily interprets Möller and Pring's observations[111] that a colloidal addition agent which lowered the surface tension of the electrolyte, and according to the bubble theory, should lower the overpotential also, actually raised it. The colloidal addition agent is deposited on the active areas of the electrode, leaving the less active areas exposed to function as the electrode, which consequently acquires a higher overpotential.

Rideal sums up his paper by saying that overpotential is a measure of the energy required for the desorption of hydrogen from a metallic surface. He considers that metals with low heats of desorption are catalytically active, the activity increasing with decreasing overpotentials. According to him metals with overpotentials exceeding 0.455 volt are catalytically inert and no metal can possess an overvoltage exceeding 1.80 volts.

Attempts of this sort are to be welcomed; but this particular one does not seem to have been very successful. Rideal is comparing overvoltage at room temperature with catalytic activity at much higher temperatures—at any rate so far as Sabatier's experiments are concerned. He includes in his discussion the oxidation of ammonia by platinum, and platinum has a high oxygen overvoltage. He postulates that a low heat of adsorption means high catalytic activity and ignores the fact that the heat of adsorption of hydrogen by platinum is apparently much higher than the heat of adsorption of hydrogen by charcoal, although the catalytic activity of platinum for hydrogenation is much greater than that of charcoal. It is true that the two heats of adsorption were determined at different temperatures and that probably neither of them is very accurate; but the data should have been mentioned and explained away if possible. Since adsorption and desorption are dynamic and not static phenomena, it is not clear why lead, mercury, and zinc, which have overvoltages, should not activate hydrogen to some extent.

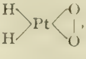
A more plausible line of attack would seem to be that platinum catalyzes the reaction[112] between atomic and molecular hydrogen; but establishes an equilibrium with some monatomic hydrogen remaining. This accounts for the low overvoltage[113] and the distinct activation. Lead, mercury, and zinc do not catalyze the reaction; but the equilibrium lies entirely at the stage of molecular hydrogen. This accounts for the high overvoltage and the low catalytic action. The other metals come in between these two extremes and at higher temperatures, the activating power of nickel and copper for hydrogen becomes greater than that of platinum. This set of hypotheses accounts for many facts because devised for that purpose; but there is as yet no independent proof. According to this point of view there is no necessary relation between overvoltage and catalytic activity. The first depends upon the slowness with which equilibrium is reached and the second on the point at which equilibrium is reached, two entirely different things.

Fink[114] has recently done some very interesting work involving electrolytic contact catalysis for which no satisfactory explanation is forthcoming as yet. When a copper sulfate solution is electrolyzed with an insoluble anode, there is a great falling off of current efficiency if there is much iron in the solution[115] because the ferrous sulfate is oxidized to ferric salt at the anode and reduced back at the cathode. If a graphite anode is used and if sulfur dioxide is passed into the cell, the ferric sulfate is reduced rapidly and practically completely to ferrous sulfate, presumably according to the equation

$$Fe_2(SO_4)_3 + H_2SO_3 + H_2O = 2FeSO_4 + 2H_2SO_4$$

In other words, the oxidation of sulfurous acid to sulfuric acid takes place in presence of ferric ions. The graphite is also essential in order to bring about a rapid oxidation and to eliminate entirely the anodic evolution of oxygen. If a ferrosilicon anode is substituted for the graphite one, the evolution of oxygen increases rapidly. Neither graphite alone nor ferric sulfate alone will affect appreciably the rate of oxidation of sulfurous acid to sulfuric acid. The combined effect of the two catalyzers is necessary.

At this point it may be well to refer to the experiments of Rupert[116] who has confirmed and extended the experiments of Wigand[117] on oxyhydrogen gas. The order of catalytic action is: palladium, platinum, cobalt, gold; silver, copper, lead, tin, nickel, iron, chromium, tungsten, manganese, aluminium, and bismuth have practically no catalytic action. The four metals have their catalytic action increased by anodic polarization, the magnitude of the activities of the metals being then approximately: Pd, 10,000; Pt, 200; Co, 10; Au, 1. There are at least two possible explanations. Rupert inclines to the view suggested by Marie[118] that with platinum the oxide PtO_2 has catalytic power. This probably means alternate reduction and oxidation. It is possible, however, that we have reduction and that then the reaction takes place at the interface between platinum and the oxide, whatever it is. Willstätter and Waldschmidt-Leitz[119] have shown that hydrogenation with platinum takes place more readily in the presence than in the absence of oxygen. They consider that the active intermediate stage is



, or some derivative of this. In so far as the oxygen is essential to the hydrogenation, anything that removes the oxygen will act as a poison to the catalyst. They suggest that glycerol and thiophene act in this way.

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[111] *J. Chem. Soc.*, **105** (1914), 712.

[112] Lewis and Jackson, *Proc. Am. Acad. Arts Sci.*, **41** (1906), 412.

[113] Bennett and Thompson, *J. Phys. Chem.*, **20** (1916), 296; Bancroft, *Ibid.*, **20** (1916), 396.

[114] Unpublished work reported at the 61st Meeting of the American Chemical Society, Rochester, N. Y., April 26 to 29, 1921.

[115] Bell, *J. Phys. Chem.*, **7** (1903), 652, Kern, *Trans. Am. Electrochem. Soc.*, **33** (1918), 83.

[116] *J. Am. Chem. Soc.*, **42** (1920), 402.

[117] *Sitzb. Ges. Naturwiss. Marburg*, **1907**, 33.

[118] *Compt. rend.*, **145** (1907), 117; **146** (1908), 475; *J. chim. phys.*, **6**, (1908), 596.

[119] *Ber.*, **54** (1921), 113.

Taylor and Neville have studied the effect of certain catalytic agents on the interaction of steam and carbon, using various forms of carbon. The interaction of carbon dioxide and carbon is accelerated by the same substances which accelerate the reaction between steam and carbon, while ferric oxide is ineffective with both, though a good catalyst for the water-gas reaction. Adsorption measurements show that substances which accelerate the reaction between carbon and carbon dioxide and the one between carbon and steam increase the adsorption of carbon dioxide by charcoal.

DISPLACEMENT OF EQUILIBRIUM

At Johns Hopkins University, Reid has obtained a result of extraordinary importance if there is no error in his results. He passed equimolecular volumes of alcohol and acetic acid over silica gel at 100°. At this temperature the equilibrium corresponds to about 67 per cent formation of ethyl acetate; yet for long periods a yield of 76 per cent and over was obtained. There is nothing theoretically impossible about a displacement of equilibrium;[120] but this is the first bit of experimental evidence to that effect and consequently it is essential that this result should be verified. It has been suggested by Mr. Taylor that equilibrium may not be reached in the vapor phase at the same point as in the liquid phase.

SUMMARY

While this report suggests many minor problems it is clear that the two fundamental things to be done next in the study of contact catalysis are:

1—To determine in what cases definite intermediate compounds are formed and what they are.[121]

2—To determine what bonds and contravalences are opened when adsorption takes place, and to show that the opening of these bonds and contravalences accounts for the formation of the reaction products.[122]

APPENDIX

This conception of contact catalysis takes out the mystery and makes it clearly a special case in the general problem of nonelectrolytic reactions. The precipitation of barium sulfate, for instance, from mixed solutions of barium chloride and sodium sulfate is apparently quite simple theoretically. The barium ions and the sulfate ions are the active masses and they combine with neutralization of the charges and precipitation of the sparingly soluble barium sulfate. There are not necessarily any intermediate stages so far as we see now. Supposing we take the reaction between quicklime and water vapor as a somewhat more complicated case. Both are saturated compounds in the ordinary sense of the term and they react to form calcium hydroxide. In order for these to react, some regular bonds must break or some contravalences must open up. Does water vapor contain infinitesimal quantities of hydroxyl and monatomic hydrogen, either electrically charged or not and do these react with the quicklime? Does the oxygen of the water, of the lime, or of both become quadrivalent and then react, or does one of the bonds between the calcium and the oxygen break, forming –Ca–O–? We have seen that, under the influence of light, oxygen may oxidize dyes or that dyes may reduce oxygen, and that the two cases are not identical. Should we say that lime reacts with water, water with lime, or does each react simultaneously with the other?

The case of lime and water is probably not an easy one to study experimentally because of the great difficulty in determining the intermediate stages and it will probably be wiser, just as in contact catalysis, to study organic reactions. When two saturated organic compounds react, one preliminary stage must be either a dissociation of one or both of the reacting substances with the breaking of regular bonds, or the formation of an addition compound with subsequent rearrangement. The formation of an addition compound will often, though not necessarily, involve the opening of contravalences. In this country Nef was the great proponent of the dissociation hypothesis and Michael is of the addition hypothesis. Both men could not be right and nobody knows to what extent either is right. Fry belongs to Nef's school; but he insists that all compounds are polar, an assumption which is not accepted by G. N. Lewis, for instance. Langmuir has shown that at high temperatures hydrogen dissociates to electrically neutral, monatomic hydrogen, which is a very reactive substance. That does not preclude the intermediate formation of positively and negatively charged monatomic hydrogen; but it makes it possible that reductions by hydrogen gas are not ion reactions. As has been stated in the body of the report, Baly in England has been working at the general problem of activation; but it is of such fundamental importance that every chemist in the world, and especially every organic chemist, should be keeping it in mind so as to be ready to do his share toward the solution.

The first thing to be done is for somebody to go over the work of Nef, Michael, and their successors critically, so as to determine just what facts have been established, and what is needed to fill in the gaps. It is probable that it would then be possible to formulate some general conclusions which would be of assistance to the organic chemists.

A second line of attack is through photochemistry. We know that only that light which is absorbed can produce chemical reactions and we also know that, of two absorptions bands, the light corresponding to one may be much more effective in causing a reaction than the other. We do not know, however, whether in these cases the light corresponding to the second band is less effective in activating the substance in the same way or whether the less effective light tends to produce an entirely different reaction. Suppose, for instance, we mordant a basic dye with a substantive dye of a different color. Light of one wave length will make the basic dye oxidize more readily and light of another wave length the substantive dye. In the case of dyes we can locate the absorption band with reference to certain chromophoric groups with some degree of accuracy; but there is very little known in general in regard to absorption bands and particular bonds in the molecule. It might be possible, for instance, to start with monochlorobenzene and to convert it practically completely into the *o*-, *m*-, or *p*-dichloro compounds as desired, by the use of proper wave lengths in connection with a chlorine carrier. The formation of methyl mercuric iodide in sunlight seems to involve the dissociation of methyl iodide into methyl and monatomic iodine, both of which then react with mercury; but nobody has shown definitely that the activating wave lengths are or are not those which are adsorbed by methyl iodide.

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[120] J. J. Thomson, "Applications of Dynamics to Physics and Chemistry," **1888**, 203, 234; Bancroft, *J. Phys. Chem.*, **21** (1917), 580; **22** (1918), 433.

[121] Mr. Bray believes that this is a practical impossibility in most cases. "We can prove in many of these cases that a given substance is a possible intermediate step, or that two reactions, such as the reduction of an oxide catalyst by carbon monoxide alone and the reoxidation by oxygen alone, take place sufficiently rapidly to account for the catalysis. In general, however, we cannot prove that in the actual catalysis this definite compound is the actual intermediate state, or that the two definite reactions postulated actually take place. Any set of intermediate reactions that can take place more quickly will do so and will be the actual mechanism.

"In spite of this difficulty, the chemical theory of catalysis seems to me to be a very powerful weapon. We can often use it even now in selecting the most probable catalysts for a given reaction. The difficulty seems less serious if we admit that there is usually no fundamental difference (as far as catalysis is concerned) between definite and indefinite intermediate compounds."

Mr. Bray suggests the alternate form: "To determine what compounds, definite or indefinite, may be possible intermediate steps."

[122] Mr. Bray suggests that the Lewis theory of valence will be useful here for "if we stress the idea that, in general, a bond consists of two electrons held jointly by the two atoms in question, we have a theory that applies equally well to the definite and indefinite compounds."

A third line of attack is through contact catalysis as indicated in this report. It was originally planned to postpone the discussion of the general problem until the second report of the Committee; but the problem as a whole is so much larger than the contact catalysis part that it seems wiser for the Committee on Contact Catalysis to stick to its own job and to turn the larger problem over to a committee to be selected with special reference to the work to be done.

Early References Pertaining to Chemical Warfare[1]

By C. A. Browne

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Among recent discussions in European chemical journals at the present time is a dispute as to whether the proposition to use poison gases as a weapon of attack originated with civilians or with the military authorities. According to a statement by Professor Haber, no one in the German army either previous to the recent war or during the first months of the conflict had conceived the idea of using poison gas or had made experiments for such a purpose. This statement, which Sir Edward Thorpe accepts as true in a recent issue of the *Journal of the Society of Chemical Industry*,[2] would seem to give the credit or blame for the idea to persons not in the military service. If this view is correct it simply repeats what has taken place in the history of chemical warfare from the time of the invention of Greek fire down to the present day. A few references in confirmation of this will be cited.

The first reference is from Wemyss Reid's "Memoirs and Correspondence of Lyon Playfair."[3] Lord Playfair, who studied under Liebig at Giessen, writes thus in connection with his work of organizing the Department of Science at the Royal College:

> It was fortunate that the Department of Science and Art was founded in 1853, because the Crimean War broke out in the following year and heavily taxed the country. At the beginning of the war I wrote a letter to the Prince Consort which he forwarded to the Master of the Ordnance, suggesting one or two applications of science to the purposes of war. One was a hollow, brittle shell containing phosphorus dissolved in bisulphide of carbon for the purpose of producing conflagration of the enemy's stores or property. The shell contained antimony, so as to make it break on a hard surface. It then scattered the liquid over the objects to be burned, and each drop, on drying, started a new center of conflagration. As the fumes of phosphorus are apt to put out their own flame, a little beeswax or petroleum was added to prevent this. The Ordnance Department reported against this proposal, and I did not care to push it further; but ten years later the plan with exactly the same materials was adopted, and the inventor, who was an officer, received promotion, and I think a decoration. The Fenians have lately used this method of setting property on fire, and tried its effect on one of the Cunard ships.
>
> The other proposal in my letter was to have a hollow, brittle shell containing cyanide of cacodyl. This is an intensely poisonous substance, a few drops of which in a room would poison the occupants. Such a shell going between decks of a ship would render the atmosphere irrespirable, and poison the men if they remained at the guns. This suggestion was considered inadmissible by the military authorities, who stated that it would be as bad a mode of warfare as poisoning the wells of the enemy. There was no sense in this objection. It is considered a legitimate mode of warfare to fill shells with molten metal which scatters among the enemy, and produces the most frightful modes of death. Why a poisonous vapor which would kill men without suffering is to be considered illegitimate warfare is incomprehensible. War is destruction, and the more destructive it can be made with the least suffering the sooner will be ended that barbarous method of protecting national rights. No doubt in time chemistry will be used to lessen the sufferings of combatants, and even of criminals condemned to death. Hanging is a relic of barbarism, because criminals might be put to death without physical torture.

An earlier reference to the use of phosphorus in incendiary bombs, than that proposed by Playfair, is contained in the unpublished reminiscences of Benjamin Silliman, Sr., preserved in the library of Yale University. Silliman worked in 1806 in the laboratory of Frederick Accum in London and in his reminiscences of this celebrated chemist narrates the following:

> Accum assured me that he had been employed by the government to contrive some infernal machination with which to blow up and burn the French Flotilla then assembled at Bologne for the invasion of England. He accordingly arranged phosphorus and chlorate of potassa in contiguous divisions of tin canisters. These were to be projected upon the flotilla and the contrivance was such as to mingle, in the act of discharge, these most explosive materials which if once in contact with the ships would destroy them by explosion and by a fearful combustion which nothing but submersion could extinguish. Happily the project failed—the canisters exploded in the air short of their object and as the flotilla never left the harbor all was well in the end—while Trafalgar dissipated the dream of French invasion.

Those who have read Lippmann's[4] "Essay upon the History of Gunpowder" or Hime's book upon this subject will recall that the introduction of gunpowder to European nations was due largely to Roger Bacon, who was a friar, and to Albertus Magnus, who was a bishop. Bacon spoke of it as composed of "*salis petrae, lura nope cum urbe et sulphuris*," the words *lura nope cum urbe* being the anagram for *carbonum pulvere* or powdered charcoal. It is strange that Bacon should have used an anagram to conceal the most common of the ingredients. Gunpowder was known to the Arabs and Byzantine Greeks who used it for rockets, fire balls, and pyrotechnics, but not for loading firearms. Its use for the latter purpose was the discovery of Berthold Schwarz, a German monk, shortly before the year 1300.

The flame projectors used in the recent war do not seem to have created half the terrifying effect produced by the dragon-mouthed siphons which ejected the liquid fire invented by the old Greek architect Callinicus in 678 A. D. The composition of this Greek fire was a secret jealously guarded by the Emperors of Constantinople for many centuries, but it is now supposed to have contained naphtha and quicklime as its principle ingredients, with a certain amount of sulfur and pitch. This mixture, it is stated, when wet with water evolves so much heat from the action of the lime that the naphtha and other ingredients are ignited.

It is thus seen that what a Greek architect and several monks in the middle ages accomplished in the way of contributions to warfare has been continued in more recent times by the chemists. The arts of piety and peace have thus helped to increase as well as to mollify the horrors of war. Generals, grand marshals and the military class, as a whole, have contributed little or nothing in the way of great discoveries or inventions in warfare. In the cases where they do claim credit for such a discovery it usually turns out, as in the incident cited by the chemist Playfair, where an officer was decorated and promoted for a proposal which Playfair himself had made ten years before. Thus again is verified the old saying that the professional militarist is not only the most brutal but the most stupid of mankind!

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[1] Read by title before the Section of History of Chemistry at the 63rd Meeting of the American Chemical Society, Birmingham, Ala., April 3 to 7, 1922.

[2] *J. Soc. Chem. Ind.*, **41** (1922), 43r.

[3] Harper and Bros., New York, **1899**, 159.

[4] "Abhandlungen und Vorträge," **1906**, Vol. 1, 125.

Study of Chemical Engineering by the Unit-Operation Method[1]

By **W. K. Lewis** and **R. T. Haslam**

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The School of Chemical Engineering Practice, as established by the Massachusetts Institute of Technology, gives the student practice in applying previously learned theory to the "unit operations" into which the field of chemical engineering is divided. The two primary unit operations are flow of fluids and flow of heat, while the secondary unit operations are evaporation, distillation, filtration, extraction, combustion, drying, etc. It is felt that not only is it necessary for the student to have a knowledge of the fundamentals of the science but that he also must have training in the use of this knowledge. Instruction in the application of knowledge is effectively given by using industrial plants as laboratories of chemical engineering, since the work is not stereotyped and may be made to develop resourcefulness and judgment in the student.

BEFORE considering the study of chemical engineering by the unit-operation method as carried out in the School of Chemical Engineering Practice of the Massachusetts Institute of Technology, it will be necessary to give a brief description[2] of this School, together with the methods employed in teaching chemical engineering by experimental work on full scale operating equipment.

SCHOOL OF CHEMICAL ENGINEERING PRACTICE

At three industrial centers, the Massachusetts Institute of Technology has established field stations of the School of Chemical Engineering Practice, each station having access to two or more industrial chemical plants. Here the student studies the practice of his profession and carries out quantitative tests on the process and equipment to determine their efficiency and how they may be improved. As the attendance is limited, there are never more than twelve students at a time at one station and these men are under close supervision of a member of the Institute Faculty and his assistant who devote their entire time to the educational work of the station. After graduating from the usual four-year course at the Institute or any other school of recognized standing and therefore being well grounded in the principles of general inorganic and organic chemistry, analytical chemistry, physical chemistry, and chemical engineering, the student spends six months in the School of Chemical Engineering Practice, where the work is confined to teaching him how to use this knowledge in the plant. By means of experimental work on full scale equipment and the application or comparison of theory and practice there are fixed more firmly in the student's mind the fundamental factors of chemical engineering and this knowledge is rendered more available for future use. Although the plants which coöperate with the Institute cover a wide field of industrial chemical processes, namely, the manufacture of sulfite and soda pulp, writing-paper, caustic soda, chlorine, heavy chemicals and acids, rubber, sugar, iron, steel, gas, coke, benzene, ammonia, soap, etc., the majority of the time in the Practice School is not spent on the study of industrial chemistry but on the study of chemical engineering which the manufacture of these materials illustrates.

PRIMARY AND SECONDARY OPERATIONS

The field of chemical engineering has been divided into unit operations and the particular industries coöperating in the work have been so chosen that in them we find numerous examples of each. A list of these unit operations may be found in THIS JOURNAL,[2] although this list has been slightly enlarged and modified during the past year. The two basic or primary unit operations are, first, the flow of fluids (liquids and gases) and, second, the flow of energy, usually in the form of heat. Those secondary unit operations which are of next importance are evaporation, distillation, drying, combustion, filtration, extraction, etc.

BROAD SCOPE OF THE PRIMARY UNIT OPERATIONS

The primary unit operations, flow of fluids and flow of heat, are of utmost importance to every chemical engineer. They provide the means for carrying out or controlling almost all industrial chemical processes since the rate of reaction, the yield and the efficiency of a process are usually regulated by the rate at which material or heat energy is put into or taken away from the system. Furthermore, a study of the remaining unit operations is dependent on a knowledge of these two primary unit operations. Examination, in detail, of two of the secondary unit operations reveals the intimate part the two primary unit operations play.

Consider distillation and fractionation. Heat has to be supplied to the wall of the still, passed by conduction through the walls of the still itself and into the liquid which is being distilled. The vapor from the boiling liquid passes up through the fractionating column and the liquid reflux passes down on the absorption of the right amount of heat which must pass serially through the condensing vapor film, through the material of the condenser itself, and finally through the film of the cooling fluid on the outside. Later, the final distillate must be completely condensed by another similar process of heat absorption. Throughout the entire process of distillation and fractionation an exact knowledge of the flow of fluids and the transfer of heat energy is, therefore, indispensable. This is even more emphasized when we consider the fact that any quantitative study of distillation depends on suitably equating the material and heat input with output.

Again, consider the secondary unit operation of drying, and, in particular, a subdivision of this operation, air-drying. Air has to be forced through a heater in order to pick up the right amount of heat to dry the material properly, the heated air is passed over the material to be dried, the water in the wet material is evaporated by the heat in the air, and the moisture must be carried out of the dryer by the outgoing air. The power required to force the air through the system increases with increased velocity of the air, but the cost of this is offset by the fact that increased air velocity aids in the transfer of heat from the heater to the air and also aids in the rate at which water is evaporated from the wet stock. Therefore, it is seen that both the design of an economical air-drying apparatus and its control (either from the standpoint of quality or quantity of output) depends on a thorough knowledge of the flow of fluids and the flow of heat. So with the other unit operations of chemical engineering, each may be analyzed and a proper understanding of all will be found to depend to a considerable extent on a thorough knowledge of the two primary unit operations, the flow of fluids and the flow of heat.

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[1] Presented before the Section of Chemical Education at the 63rd Meeting of the American Chemical Society, Birmingham, Ala., April 3 to 7, 1922.

[2] For a more complete description of the School of Chemical Engineering Practice see THIS JOURNAL, **13** (1921), 465, **9** (1917), 1087.

Classroom Training in the Unit Operations

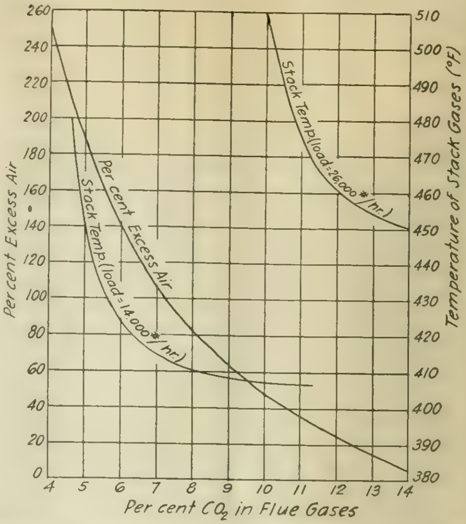
As stated above, before the student enters the Practice School, he must be well grounded on the theoretical side of both the primary and the more important secondary unit operations. This is accomplished at the Institute by means of a course extending throughout the senior year in which these subjects are treated in a quantitative, mathematical way by means of lectures, recitations, and home problems. The numerous problems are broad in scope and tax the student's imagination and judgment, giving him practice in the quantitative application of the laws and principles taken up in lecture and recitation. The instruction along these lines is thorough and exhaustive, but as in any recitation and problem course most of the necessary data must be supplied by the instructor, and, furthermore, there is a limit beyond which it is difficult for the average student to go without corresponding personal experimentation. Therefore, after the student has completed his four-year undergraduate course in Chemical Engineering which includes the above lecture, recitation, and problem work, and for the completion of which he receives the degree of Bachelor of Science, he then may elect to go into the School of Chemical Engineering Practice, where he carries out personal experimentation in the various unit operations of chemical engineering.

Experimental Work in the Unit Operations of Chemical Engineering

During the first week or so at each station in the School of Chemical Engineering Practice, the student examines in detail the plant layout, construction, and methods of manufacture. He correlates his efforts along these lines by making up a flowsheet of the process or by writing a complete report. Flowsheets are made by the student when the sequence of operation, plant layout, method of handling materials are important; a report of his detailed study is made when construction methods and the materials of construction are more important. After the student has been made familiar with the particular plant and process, he is ready for his unit operation experimental work.

The first experimental work is usually carried out by the entire group at a given station (from six to twelve students). In this way, the student quickly learns how to organize his plant experimental work, how to attack a plant problem, and comes to appreciate the difficulties of plant research and some of the precautions that must be observed to obtain reliable figures. After two or three "group tests" he is allowed to choose individual "plant investigations" in the various fields of the unit operations. It should be pointed out that in all this experimental work in the plant the Director of the station endeavors to throw on the student the entire burden of designing the test, carrying it out, and working up the results. Some men, owing either to ability or maturity of judgment, are better able to decide what data should be obtained and how, and the significance of poor results, while others with less ability along these lines have to be aided to a greater extent by the station's staff. Such individual attention is possible, since the average number of students at a station is about ten. In the period of eight weeks which the student spends at a station, he carries out experimental work in each of the unit operations assigned to that station, and he then proceeds in a like manner to the next two stations, thus in twenty-four weeks carrying out experimental work in all the more important unit operations under plant conditions, such as exist in seven large chemical industries.

In all this experimental work, it should be emphasized that the underlying motive is the application of theory, as developed in the classroom, to practice, or a comparison of calculated with observed results. Since the function of engineers is to apply science to industry, it is necessary in the training of engineers to do two things: first, teach them the fundamentals of their science, and, second, teach them how to apply it. Too often the second function has been ignored and the assumption made that if a student knew the fundamentals he could find out by experience how to apply them. Not only is this incorrect, but it is usually true that it is much *easier* for the average student to *absorb* knowledge than it is for him to *apply* it.



Per cent Excess Air and Stack Temperatures *vs.* Per cent CO_2 in Flue Gases

Experimentations in Plant vs. Experimentation in Laboratories

Here the question might well be raised why plant experimental work is considered necessary and why we are not content to have the student carry out experimental work on a laboratory scale only. Consider the primary unit operation, flow of fluids. It is easily possible to arrange a series of laboratory experiments measuring the flow of gas and liquid streams by means of orifices, pitot tubes, etc., and from such work the student obtains information and training of much value. However, the laboratory apparatus is practically all set up for him, even the location at which the orifice or pitot tube must be inserted is evident from an inspection of the equipment, and the student has no opportunity either to *design* his test or to exercise any judgment as to the most suitable method. He does *not* decide what instrument or what particular point for measurement is best suited, nor does he develop the resourcefulness necessary to obtain this measurement under plant conditions of inaccessibility and continuity of production.

The particular example of experimentation just given is of the simplest sort and such work can be made much more effective in technical laboratories than experimental work in the more complicated unit operations. As carried out in the School of Chemical Engineering Practice, the student would meet the above problem as a subdivision of a larger problem, and his first decision would be that this particular stream of material had to be measured in order to obtain necessary data for the main problem. Next he would have to decide on his method of measurement, taking into consideration the accuracy needed in connection with the problem, as a whole, and how the apparatus could be installed to give satisfactory results without seriously interfering with plant production. In plant experimentation, conditions are such that the student develops technical judgment and mental resourcefulness, whereas in the chemical engineering laboratory the experimental difficulties are much less and fail to develop the student properly. Furthermore, the student has to find out for himself at some later date the difficulties of repeating his laboratory methods in the plant and how to work effectively under such changed conditions. Many other points, such as cost of equipment and cost of operating such equipment, might be brought up against confining the chemical engineer's training to class and laboratory work, but we believe a sufficient number of points have been brought out to show the superior effectiveness of plant experimentation.

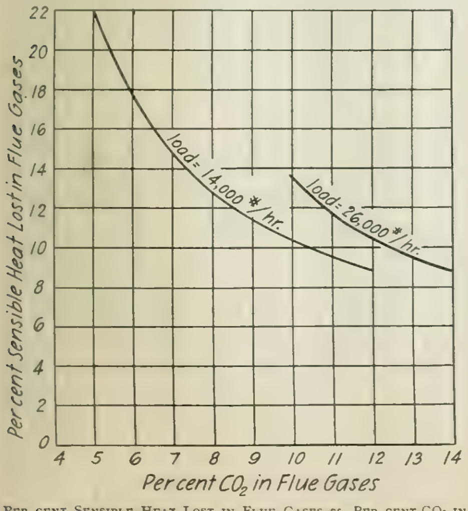
ILLUSTRATIONS OF EXPERIMENTAL METHODS AND RESULTS

Having seen how the field of chemical engineering has been subdivided and the general method by which the students attack plant research problems, a few details and illustrative results on several of the unit operations may be of interest.

COMBUSTION—In view of the wide use and importance of fuels in all industries, considerable attention is given to the study of the secondary unit operation combustion. In the Practice School many facilities are available for studying this important phase of chemical engineering, consisting of hand and stoker fired boilers burning coal, coke breeze, fuel oil, blast furnace gas and wood waste, open-hearth furnaces and soaking pits burning producer gas generated in numerous types of producers, coke ovens burning coke oven gas, rotary kilns using powdered coal, etc. This unit operation offers one of the most striking fields for demonstrating the industrial applicability of the principles of physical chemistry, such as the law of mass action, the effect of temperature and the effect of catalysts (incandescent brick surfaces) on the rate of reaction. In studying combustion, the student also receives much training in the use and importance of the two primary unit operations, flow of heat and flow of fluids.

Figs. 1 and 2 show the summary of the results obtained by two students experimenting with a 500-h. p. boiler burning fuel oil. These men studied the effect of varying the amount of excess air, the effect of changing the distribution and mixing of the air and oil, and the effect of load on the efficiency.

Table I shows a total heat balance on a set of sixty coke ovens. It should be borne in mind that the primary educational object is not to obtain a "heat balance" but to study one of the unit operations. The comparison of the heat input and output merely gives some idea of the completeness of the data, although, of course, a check may be reached by counterbalancing errors. The measurement of the heat quantities shown in Table I gives good training in the study of the flow of fluids and the flow of heat as well as in combustion, although the main benefit of such a test lies in the power of reasoning developed in the design of the test and the practice obtained in organizing for effective work. A comprehensive test on coke ovens gives excellent training in the measurement of material and heat quantities, in gas and fuel analysis, in the study of the laws of heat radiation and convection, and in the use of industrial stoichiometry. Furthermore, to increase the efficiency of teaching in the School of Chemical Engineering Practice, all the work is "motivated," that is to say, the student is not told to carry out experimentation in the unit operation itself, but some definite and usually attainable objective, the importance and significance of which he understands, is placed before him.



PER CENT SENSIBLE HEAT LOST IN FLUE GASES *vs.* PER CENT CO_2 IN FLUE GASES

TABLE I HEAT BALANCE ON SET OF 60 COKE OVENS

INPUT

	Per cent
Coal, latent	92.82
Coal, sensible	0.01
Fuel gas, latent	7.15
Fuel gas, sensible	0.02
	100.00

OUTPUT

	Per cent
Coke, latent	61.5
Coke, sensible	3.63
Foul gas, latent	21.04
Foul gas, sensible	1.24
Tar, latent	4.84
Tar, sensible	0.22
Stack, sensible	1.29
Stack, latent	1.02
Foul gas water, sensible	..
Foul gas water, latent	0.97
Radiation	1.19
Unaccounted	3.06
	100.00

EXTRACTION—In this field there are a number of phases; let us consider the absorption of a gas by a stream of liquid traveling in opposite direction to the gas stream. The underlying principles of countercurrent extraction are studied thoroughly in class by the student before going into the Practice School, so this theory is applied to plant practice under various conditions. For example, the student applies these principles to such problems as the absorption of sulfur dioxide by milk of lime to form bisulfite cooking liquor used in the manufacture of sulfite wood pulp, to the absorption of hydrogen chloride gas by water in the manufacture of muriatic acid, to the scrubbing of light oil from coke oven gas by paraffin oil, and to the absorption of ammonia from coke oven gas by water. Knowing the equation expressing the theoretical performance of such a countercurrent extraction system, we can measure the efficiency of the extraction tower by means of a "tower coefficient." The "tower coefficient" enables the student to compare quantitatively the efficiency of various forms of tower packing, and to forecast the effect on output of a change in the temperature of the gas or absorbing liquid, of increasing the size of the tower, and of increasing or decreasing the partial pressure of the solute in the entering gas stream. Some of the "tower coefficients" determined by the students which were used by them in forecasting results under changed conditions are given in Table II. The determination of these coefficients also shows the student how small towers may be used experimentally in determining the proper size of a new installation of commercial towers.

These coefficients are all expressed as lbs. of solute absorbed per min. per cu. ft. of inside tower space per mm. of Hg driving pressure of the solute (partial pressure of solute in gas minus partial pressure of solute in solvent).

TABLE II

	TOWER COEFFICIENT $\times 10^{-6}$
So_2 absorbed in milk of lime, tile tower	85
SO_2 absorbed in milk of lime, plate tower	2160
Benzene absorbed in paraffin oil, slat tower	2240
Ammonia absorbed in water, slat tower	216

DRYING—Drying, an important secondary unit operation, is given much attention, and experimental work has been carried out by the students on coal-fired, semi-indirect rotary coal dryers, steam-heated rotary sugar dryers, steam drum dryers, can dryers for drying pulp and paper, French dryers used for drying flake soap, etc. The student is taught to find the largest resistance to the flow of heat or to the diffusion of water, to concentrate on this particular resistance and reduce it by one means or another, thereby bringing the dryer to the maximum possible capacity for the machine or stock in question. For example, a test by some students on a can dryer drying paper showed that the major resistance to the flow of heat from the steam inside the drum to the paper was the resistance between the outside face of the drum and the underside of the stock. The student could, therefore, direct his attention to the most probable point for a successful attack. Again, in the air-drying of sugar a similar method of attack showed the importance of increasing the air velocity, which made possible a considerable increase in output from the same dryer.

NOTES AND CORRESPONDENCE

Petroleum Hydrocarbons

Editor of the Journal of Industrial and Engineering Chemistry:

While reading the recent interesting paper by Dr. Van H. Manning on "The Pioneer's Field in Petroleum Research," I observed the following statement: "Our knowledge of the constituent hydrocarbons making up lubricating oils is well nigh a blank, and so much depends on the quality of those oils." For more than a year, I have been industriously engaged with the aid of several assistants on the continuation of the work described in the preliminary paper I presented before the Petroleum Section of the SOCIETY at the Rochester Meeting in May 1921, and have separated from representative samples of the world's supply of petroleum the undistillable lubricant and asphaltic hydrocarbons. Within a few months I expect to publish an account of the separation of these hydrocarbons, and their identification by specific gravity, molecular weight, and analysis, together with their index of refraction, and viscosity, and with the relations in general of specific gravity and viscosity.

CHARLES F. MABERY

CASE SCHOOL OF APPLIED SCIENCE
CLEVELAND, OHIO
May 15, 1922

The Plant Manager and the Chemist

Editor of the Journal of Industrial and Engineering Chemistry:

THE ideal chemist is the catalytic agent in a plant, furnishing and examining ideas to improve or cheapen manufacture, to produce new and desirable products, and to standardize production. Upon him rests the selection of raw materials to build up into the finished line upon which the reputation of the house rests. He is the judge of the standard to be attained by the finished product, and upon his ability to read aright the desirability of the finished article rests the whole force of the sales department. He is the leaven working through the foremen in the plant, developing a coöperative spirit of constructive criticism leading to the development and improvement of the different steps of manufacture.

The chemist and his "Lab" and his assistants are the media for the investigation and the rejection or the translation into practice of the ideas not only of his own force but of the plant manager and the other members of the manufacturing force. No person is too exalted to have his ideas carefully tested before attempting to use such ideas in manufacture, and no employee is too humble not to have his thoughts receive careful attention.

Now as a plant manager, I find that the chemist is far from the ideal. The fundamental failure of the chemist is first in a lack of knowledge—of thoroughness of education in chemical and related lines. The chemist must, first of all, know chemistry. He must be familar with modern thought and development, particularly in the chemistry involved in the type of manufacture in which he is employed. He must be a good, rapid, accurate analyst because practically all investigative and research work rests on the bed-rock of accurate analysis. One might write a volume on the failure of our universities to realize this fundamental truth in industry. And not only should a chemist be thoroughly familiar with analytical methods, he must in industry be able to secure results rapidly, for information which is quickly available is of greatly enhanced value. But above all, his conclusions drawn from analysis must be correct.

Any plant manager who has given work to chemists or commercial laboratories is familiar with the appalling lack of agreement in simple analytical determinations. Far too often, the plant manager knows the chemist is wrong and still oftener he suspects gross inaccuracy and carelessness. These poor results are not confined to graduates of secondary schools, and it would appear high time that somebody of authority should pass on a commercial laboratory's ability to do correct work in the industrial lines in which it claims to be expert.

The second great failure of the chemist has been in salesmanship. The chemist must sell himself and his ideas to the plant manager, to the superintendent, and to the various foremen. All too often, meritorious ideas are abandoned because the man actually carrying out the operations has not had the matter thoroughly clarified to him and does not give it a fair trial. If the chemist has good salesmanship, every man from the manager down will always feel that his suggestions have potential merit and no idea will get across in production without such faith. Brains must have the cordial coöperation of labor. When the chemist has the plant foremen as eager helpers, it is safe to say that he is not only a good chemist but a reasonable human being with a proper respect for men working in subordinate positions.

This leads to my third criticism that too often the chemist is seeking authority in the plant rather than responsibility. The chemist who must have personal authority to get work done by employees in a factory is about a certain failure. What a plant needs in a chemist is one who takes responsibility for progress in manufacture and does not require authority in order to secure all the coöperation he needs. To secure such help the chemist must remember that any man who is doing his work well even in a menial position takes pride in that work and is anxious to do it better but resents any trace of overbearing authority. The Golden Rule will pay a chemist greater dividends in a factory than a college education. This point in personal salesmanship, of securing cordial coöperation, is of an importance that can be scarcely overestimated in a factory. The plant manager can give the chemist much help here, but in the long run the chemist must, by his ability and fairmindedness, himself secure this willing coöperation.

It is the place of the plant manager to secure for the chemist facilities for doing good work free from unnecessary friction. The plant manager welcomes reasonable ideas properly presented—he has no time for consideration of half-investigated plans or processes and he will never tolerate the authority-seeking internal trouble maker. But he will rise up and hail as thrice blessed the thorough investigator who will show him a carefully considered and feasible plan to reduce cost, increase production, or improve quality. For to such as these do the kingdom of industry belong.

My final criticism of the chemist concerns his standing in the community and among his fellow chemists. With his educated and analytical mind he should be interested in such civic questions as milk, water and food supply, street paving, and the purchase of materials for civic purposes. He should mix with business men and other chemists and thus enlarge his vision. He should belong to and assiduously follow the publications of his national chemical society. He should have a proper appreciation of his value to the community and walk with a high head, realizing that much of the progress of civilization rests with him, his test tubes and microscope, and that despite his proneness to a lack of coöperative effort his activities are of such great importance that modern industrial manufacture without his help is unthinkable.

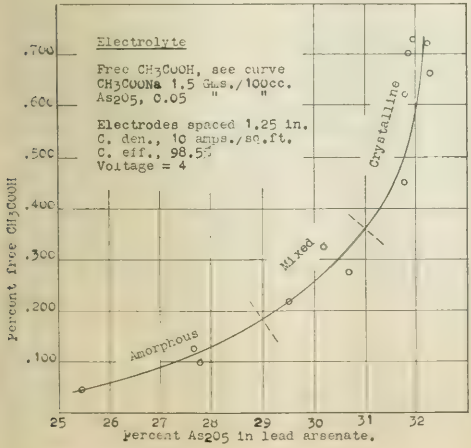
GEORGE L. O'BRIEN

O'BRIEN VARNISH CO.
SOUTH BEND, IND.
May 23, 1922

The Electrolytic Production of Lead Arsenate

Editor of the Journal of Industrial and Engineering Chemistry:

The following graph may be of interest as supplementing the data presented by Messrs. Herman V. Tartar and Gary G. Grant under the above title in the April number of THIS JOURNAL. This graph summarizes the best conditions found for the production of lead arsenate by the electrolysis of lead anodes in a bath containing sodium acetate, free acetic acid, and arsenic acid. Our choice of conditions is in very fair agreement with the independent selection of Messrs. Tartar and Grant.



The composition of the lead arsenate is controlled by the concentration of free acetic acid. The lead arsenate of the acid type was crystalline, of large dry bulk, and had good suspension quality. Lead arsenate of the basic type was amorphous, of small dry bulk, and had good suspension quality. The anodes used in our work were of bullion containing about 150 oz. silver per ton and the cathodes were sheet lead. Anodes were removed and cleaned of adhering slime once in each 24 hrs. The lead arsenate contained 0.1 to 0.3 oz. silver, although the anode slime contained about 3600 oz. per ton.

J. F. CULLEN
T. E. HARPER

U. S. SMELTING, REF. & M. CO.
MIDVALE, UTAH
May 4, 1922

Canadian Letter

By T. Linsey Crossley

208 KING ST., W., TORONTO, CANADA

At its annual meeting in Ottawa, the Canadian Institute of Chemistry shifted its presidential mantle from the academic shoulders of Professor James Watson Bain of Toronto University, to the industrial counterparts of Dr. John Seaman Bates, of the Bathurst Company, Ltd., Bathurst, New Brunswick, and in doing so recognized a leading Canadian industry, the manufacture of pulp and paper. The Institute has become in three years a vigorous organization with over two hundred fellows and associates, and a blue book.

One of the great names in Canadian industry is that of Ezra Butler Eddy of Hull, who, in 1851, started business as a lumber merchant, later adding matches, fiberware, and paper and pulp mills. In his memory Mrs. Eddy has made a bequest to establish a professorship in industrial chemistry at McGill University. It may be pointed out in this connection that McGill is well equipped for attention to forest-derived industries, being the seat of the Forest Products Laboratory of Canada.

For some years past a series of investigations has been carried on in Toronto University having to do with the toxic properties of certain compounds on microbic life. Out of this has developed lately a promising line of practical application of physicochemical methods to life phenomena. Some work on yeast indicates the possibility of progressive steps toward lethal doses as applied to organisms in disinfection.

The four lectures of Professor H. A. Lorentz of Leyden University, on invitation of the department of physics of Toronto University, constituted the notable feature of a recent symposium on light. His subject was "Light and the Constitution of Matter," and it was treated with the clarity of expression that characterizes Professor Lorentz's delivery, and made the presentation of mathematical considerations a matter of interest even to what might be termed the lay chemist. The other contributors to the symposium were Professor L. V. King of McGill University, who gave two lectures on the "Molecular Scattering of Light," and Professor J. C. McLennan, head of the department of physics, who delivered three lectures dealing with "Fluorescence and Phosphorescence," "Radiations Emitted and Absorbed by Atoms with Modified Systems of Extra Nuclear Electrons," and "Spectroscopy of Isotopes of Lithium and Other Elements."

Westward, the course of empire and chemistry is marked by the University of Saskatchewan, in letting the contract for the construction of a new chemistry building which will cost $650,000. It is not generally known that Saskatchewan is well forested and has vast lignite coal measures. The latter is of low grade and the Dominion government, acting with the authorities of Manitoba and Saskatchewan, has appropriated $400,000 for the investigations of the Lignite Utilization Board. This board is now building a commercial plant to develop the practical results of its work, which has shown that one ton of fuel briquets, almost equal to anthracite, can be made from two tons of lignite at a price to make their general use possible from Winnipeg west.

June 8, 1922

SCIENTIFIC SOCIETIES

Pittsburgh Meeting

The Pittsburgh Section is working with commendable enthusiasm toward making the September Meeting of the SOCIETY an unprecedented success. These Pittsburgh men see the full possibilities of showing chemistry intensively applied to industry, and in a manner that will grasp and hold the interest of educators, of research men, and of engineering chemists.

Accordingly, much stress is laid upon the industrial excursions that will be the principal part of the program for the last two days of the meeting. Dr. Earl Blough, of the Aluminum Company of America, New Kensington, Pa., is in charge of the excursions program, which is now about complete.

On Friday, September 8, an all-day excursion to Donora and Clairton has been arranged. At Donora zinc roasting and sulfuric acid plants and wire mill will be inspected. At Clairton, the steel rolling mill and by-product coke oven plant will be visited. A special train will take visitors to the plants and return to Pittsburgh will be made by boat, which will afford a splendid view of the industrial district.

The Council of the SOCIETY will meet on Monday at 2:30 P.M. in the "Blue Room" of the William Penn Hotel. This hotel is to be headquarters for the meeting.

Mr. R. B. Mellon of Pittsburgh has been made honorary chairman of the meeting.

One of the most interesting features of the General Meeting on Tuesday will be the address by Thomas Midgley, Jr., and T. A. Boyd of the General Motors Research Laboratories, Dayton, Ohio, on "The Chemical Control of Gaseous Detonation with Particular Reference to the Internal Combustion Engine." This address will be illustrated by experiments with an internal combustion engine on the stage and by lantern slides. The meeting will be held in Carnegie Music Hall, and for the first time a mechanical device will perform in the place of a concert singer or musician, inasmuch as use of this fine hall has never before been permitted for anything but musical events.

A large number of social and entertainment features are in preparation by Chairman J. O. Handy of the Pittsburgh Section and the Entertainment and Publicity Committees.

On Wednesday and Thursday, Divisional Meetings will be held and a number of important symposiums will be conducted.

The Division of Industrial and Engineering Chemistry will include in its program on Wednesday morning a symposium on "Automatic Process Control," under the chairmanship of L. W. Parsons.

The Water, Sewage and Sanitation Division will discuss "Specifications for Lime Water Treatment" as a feature of its meeting.

The Biological and the Agricultural and Food Chemistry Divisions will hold a joint symposium on the subject "Fatty Foods," with Dr. David Wesson as chairman. Papers dealing with the preparation, purification, digestibility, adulteration, etc., of various fatty foods are solicited for this symposium. Vitamin papers will be included.

The Rubber Division is planning the largest meeting in its history.

A Symposium on Gelatin and Collagen will be a feature of the meeting of the Leather Division.

The Dye Division is arranging a symposium on "The Chemistry of the Application of Dyes."

The Division of Physical and Inorganic Chemistry will hold a symposium on "Recent Advances in Applied Colloid Chemistry," in coöperation with the Colloid Committee of the National Research Council.

The Petroleum Section hopes to perfect its divisional organization at this meeting and will hold a short symposium on "Lubrication from the Chemist's Viewpoint."

The Section of Chemical Education is desirous of being an open forum for settling national questions in chemical education, including high school, college, university, and industry problems.

The Cellulose Section plans a number of discussions on special topics, such as "Coöperative Research Problems in Cellulose Chemistry," and "The Nature of Oxycellulose and Its Bearing on the Artificial Silk, Viscose, and Paper Industries."

The preliminary program will be mailed to members of the SOCIETY from the Secretary's office on July 20.

INDUSTRIAL DIVISION

At the present time there is no up-to-date list of members of the Industrial Division. In order that the files may be corrected it is suggested that those who would like to be upon the Division's roll should send their names and addresses to the Secretary.

Members who are preparing papers for presentation before the Division at the Pittsburgh Meeting (September 4 to 9) were asked last month to send their abstracts at the earliest possible date. Some have already done this, and if this continues it will be possible to send to each member of the Division a mimeographed copy of all abstracts of papers to be given at Pittsburgh. Better discussion of papers will result by this plan.

Professor Parsons of Massachusetts Institute of Technology is chairman of the Automatic Process Control Symposium which will be held Thursday morning, September 7. The fundamentals underlying the different practical control methods will be presented by a series of illustrated papers.

Send in name and address to the Secretary, Erle M. Billings, Eastman Kodak Co., Rochester, N. Y., to-day. Also send your abstract. Don't delay!

ORGANIZATION OF GAS AND FUEL SECTION

The new Gas and Fuel Section of the SOCIETY, authorized at the Birmingham Meeting, will hold its first session at the Fall Meeting in Pittsburgh, Pa.

Dr. A. C. Fieldner, Superintendent and Supervising Fuels Chemist of the Pittsburgh Experiment Station of the U. S. Bureau of Mines, has been appointed chairman, and Mr. R. S. McBride, of Washington, D. C., has been appointed secretary of the Section. The officers of the new Section are sparing no efforts toward preparing a program of papers that will be of special interest to gas and fuel chemists, and engineers. A large attendance is expected, as Pittsburgh is the center of this industry.

The first meeting of the new Section will include a Symposium on Combustion, under the chairmanship of Prof. R. T. Haslam, Massachusetts Institute of Technology.

SECTION OF CELLULOSE CHEMISTRY

Those who plan to present papers before the Cellulose Section at the Pittsburgh Meeting are urged to send titles, and particularly abstracts, to the Secretary, G. J. Esselen, Jr., 248 Boylston St., Boston, as soon as possible.

RAILROAD RATES

Reduced rates to the meeting are a certainty. In view of expected large attendance the railroads have agreed to sell round trip tickets at one and one-half fare on the identification certificate plan, applicable to all parts of the United States east of Arizona, Nevada, Washington, and Oregon. Tickets may be purchased September 2 to 8 on presentation of an identification certificate and will be good returning until midnight September 15. From Colorado (except Julesburg), Idaho, Montana, New Mexico, Utah, Wyoming, Oklahoma, and Texas the limits are September 1 and 16. Round trip tickets have been granted on the same plan from all territory in the Canadian Passenger Association Eastern Lines. Tickets must be validated at Pittsburgh between September 6 and 15 by agents at the regular ticket offices of the lines over which tickets read into Pittsburgh. When validated they will be good for return leaving on any day within the final limit. Passengers must reach original starting point within the transit time shown on the ticket, and in no case later than midnight of September 15, or, as stated above, September 16.

A few minor railroads do not come within these associations. If one has difficulty in purchasing a ticket locally he should pay local fare to the nearest central point and purchase a round trip ticket there.

In order to obtain this reduced fare members must secure from the Secretary of the SOCIETY an identification certificate to be presented at the ticket office when purchasing the ticket. After August 15, a limited number of these certificates will be placed with the secretaries of Local Sections to meet belated inquiries. No reduction can be obtained unless an identification certificate is obtained in advance, and no certificates obtained at local stations under the usual certificate plan are good. Certificates may be obtained for members of the SOCIETY and dependent members of their families. One certificate will serve for both traveling together.

From Pacific Coast states, round trip summer season tickets are purchasable to Pittsburgh and eastern points at approximately one and one-fourth one way fare to August 31, and good returning until October 31, 1922. These fares require no identification certificate, and stopovers are allowed.

Calendar of Meetings

American Pharmaceutical Association—70th Annual Meeting, Cleveland, Ohio, August 14 to 20, 1922.

American Chemical Society—64th Meeting, Pittsburgh, Pa., September 4 to 9, 1922.

Eighth National Exposition of Chemical Industries—New York, N. Y., September 11 to 16, 1922.

American Electrochemical Society—42nd Meeting, Montreal, Canada, September 21 to 23, 1922.

Technical Photographic and Microscopic Society

At the meeting of the Technical Photographic and Microscopic Society, held in New York on June 14, an address was made by the President, Mr. John H. Graff, on the increasing importance of photography in commercial and technical fields and on the need of a society to represent the common interests of all engaged in the work. Several members spoke briefly on the usefulness of photomicrography in industrial research.

At this meeting a constitution and by-laws were adopted. At the next meeting, to be held in September, officers will be elected for the coming year.

The New Haven Meeting—Spring 1923

The following executive committee has been selected by the New Haven Section to arrange for the meeting of the SOCIETY in New Haven in April 1923: Treat B. Johnson, Yale University, *Chairman;* Blair Saxton, Yale University, *Secretary;* Champion H. Matthewson, Yale University; Arthur J. Hill, Yale University; Ralph Langley, Acme Wire Co., New Haven, Conn.; J. E. Graveley, Winchester Repeating Arms Co., New Haven, Conn.

The Connecticut Valley Section has accepted the invitation of the New Haven Section to act as joint hosts to the SOCIETY at the meeting and several members of this Section will be added to the executive committee. Subcommittees will not be appointed until after the opening of Yale University, early next fall.

The new Sterling Chemical Laboratory will be formally dedicated by the University during the meeting.

Local Section Officers

At a meeting of the Syracuse Section of the SOCIETY on May 12, the following officers were elected for the ensuing year:

President: A. C. HOUGHTON, Semet-Solvay Co.
Vice President: R. A. BAKER, Syracuse University.
Secretary: W. B. HICKS, 127 Stinard Ave.
Treasurer: L. C. JORDY, 505 Van Buren St.
Local Councilor: C. W. EASLEY, Syracuse University.
National Councilors: R. S. FLEMING, L. E. WISE.

The new officers of the Indiana Section are:

President: H. E. JORDAN, Superintendent of Filtration, Indianapolis Water Co.
Vice President: CARL E. STONE, Van Camp Packing Co.
Secretary-Treasurer: WILLIAM HIGBURG, Republic Creosoting Co.
Executive Committee: EDGAR B. CARTER, Swan-Myers Co.; H. E. CORY, Western Oil Refining Co.; WALTER JAMIESON, Eli Lilly & Co.

The recently elected officers of the Virginia Section are:

Chairman: GRAHAM EDGAR, University, Va.
Vice Chairman: ROBERT F. MCCRACKAN, Medical College of Virginia, Richmond, Va.
Secretary: W. G. CROCKETT, Medical College of Virginia, Richmond, Va.
Councilors: GARNETT RYLAND, W. F. RUDD.

Morgantown members of the SOCIETY met in the chemistry building of West Virginia University on Friday evening, May 12, to elect permanent officers of the recently formed Northwestern Virginia Section of the SOCIETY. The section consists of thirty-four members. The following officers were elected:

President: F. E. CLARK.
Vice President: W. W. HODGE.
Secretary-Treasurer: E. P. DEATRICK.
Councilor: H. G. KNIGHT.

Correspondents in Local Sections

The following men have been appointed by the Sections as staff correspondents of the JOURNAL, and will serve to keep the editorial office in touch with the interests and activities of the Sections which they represent:

Ames: V. E. NELSON
Columbus: C. W. FOULK
Connecticut Valley: GEORGE F. TAYLOR
Cornell: F. H. RHODES
Detroit: H. C. HAMILTON
Eastern New York: E. H. DARBY
Indiana: FRANK B. WADE
Lexington: J. A. GUNTON
Louisiana: C. S. WILLIAMSON, JR.
Michigan Agricultural College: H. D. LIGHTBODY
New Haven: W. T. READ
Northern Indiana: WILLIAM J. GROSS
Northeastern: R. E. WILSON
Philadelphia: E. F. HICKS
Pittsburgh: E. J. CASSELMAN
Purdue: F. O. ANDEREGG
Southeastern Texas: H. B. WEISER
Southern California: H. L. PAYNE
Syracuse: W. M. BOOTH
University of Michigan: CLAIR UPTHEGROVE
Virginia: W. F. RUDD
Western New York: E. K. STRACHAN

Dr. R. P. Fischelis has been appointed the representative of the New Jersey Chemical Society in a similar capacity.

A Unique Meeting

A unique meeting, especially designed to care for the interests of the young men and women who are to graduate in chemistry at the end of the present semester, was held by the Indiana Section of the SOCIETY recently. The idea was conceived by Mr. H. E. Jordan, Superintendent of Filtration of the Indianapolis Water Co., who managed the meeting. All the professors of all the colleges in the state were invited to come with as many of their senior students as possible to the special meeting. About 250 took advantage of the opportunity. The new Purdue Section of the SOCIETY coöperated with the Indiana Section in making the meeting a success.

A splendid industrial chemical exhibition was arranged, showing, among other things, the series of products produced by a by-product coke oven plant and a selected series of dyestuffs and intermediates from one of the coal-tar products such as naphthalene. Medicinals from coal-tar products were also exhibited, and a series of corn products and cellulose products made another interesting group. Petroleum products illustrating the processes involved in the making of a straight-run gasoline were also shown. The students and professors were taken on several trips to industrial chemical plants.

A luncheon was followed by a spirited talk by Mr. Otto Eisenshiml of Chicago, on "Come Out of the Kitchen." Mr. Eisenshiml's thesis was to the effect that chemists did not capitalize their knowledge as much as they should. He advocated going into chemical industry and competing with those who now utilize the knowledge of the chemist and pay him a niggardly fee. The students were told by Mr. Eisenshiml that jobs in laboratories were going to be scarce this year because of the business depression but that opportunities to make money by using their knowledge of chemistry were always abundant if they would but seek them. Many cases of money making chemical enterprises were cited by Mr. Eisenshiml.

Dr. Edgar F. Smith, our honored president, was present at the meeting and addressed a group of faculty men in the afternoon and made a brief speech at the luncheon. Governor McCray of Indiana honored the Section with his presence at the luncheon and spoke to the members and guests.

The banquet in the evening was largely attended. Dr. Smith was the principal speaker, giving his address on "The Spirit of American Chemistry." Dr. Clowes, research man of Eli Lilly and Co., gave the young students an eloquent and inspiring address in the afternoon, on the choice of research as a career. His suggestions, while not disregarding a decent and suitable livelihood, led more to a life of service and of mental compensations than did the more utilitarian teachings of Mr. Eisenshiml. The young people were thus given both sides of the question upon which to ponder.

The chemical exhibit was kept for a week at the Chamber of Commerce, and for two weeks longer it was at the central public library.

Possibly other Sections may wish to do something along this line for the students and professors of their regions. From our experience in Indiana we can heartily recommend it as both pleasant and profitable.

FRANK B. WADE

SHORTRIDGE HIGH SCHOOL
INDIANAPOLIS, IND.
May 11, 1922

Meeting of the Iowa and Ames Sections

A joint meeting of the Iowa and Ames Sections of the SOCIETY, functioning as the Chemical Division of the Iowa Academy of Science, was held at Drake University, Des Moines, Iowa, on April 28 and 29. The program included twenty-four papers, covering many branches of chemical research.

Report on Standardization of Sizes and Shape of Apparatus—II[1,2,3]

By W. D. Collins

CHAIRMAN, COMMITTEE ON GUARANTEED REAGENTS AND STANDARD APPARATUS

THE recommendations given below cover the second year' work of the Committee on Guaranteed Reagents an Standard Apparatus on elimination of apparatus. Information in regard to the quantities of the different items tha are purchased by laboratories throughout the country has bee furnished by the Committee on Standardization of the Association of Scientific Apparatus Makers of the United States o America.

The recommendations are made on the basis of providing list of apparatus to be kept in stock by dealers who expect t furnish prompt service for the regular needs of chemical laboratories. Many items needed by nearly all laboratories are required in such small quantities that the total demand in th United States could easily be handled by one firm. Such item are omitted from the regular stock list with the expectation tha some dealers will have them. Certain pieces, particularly thos requiring special workmanship, will be carried in stock by manufacturers and dealers who agree that the items should be omitte from a general stock list.

This report carries recommendations on all the articles considered by the Committee. It is not possible that errors o judgment have been avoided entirely. The report is the bes guess of the Committee in the light of the combined experienc of the members and such information as has been gathered fron various sources. The Committee will welcome criticism of th report and suggestions for useful changes. It must be remembered, however, that a considerable proportion of the item discontinued have been put in catalogs because some individua has assumed that his desire for a particular article represente a universal need. Other chemists have not appreciated th special form of apparatus and another dead item has been adde to those which one dealer lists because he sees it in the catalo of another and thinks there is a demand for it.

For consideration of the Committee the apparatus was identified by catalog numbers. These could not well be printed s there may be a little uncertainty as to just what some of the item are. The Committee would not have known a number of ther without the catalog illustrations. All catalogs take up mos topics in the same order so that with a catalog at hand almos any piece of apparatus can be identified from the descriptior Information in regard to any specific piece can be obtained fron many dealers or from the chairman of either of the committee coöperating in the preparation of the report.

This report is in general confined strictly to questions of size and shapes. Therefore it does not contain many recommendations in regard to the kind of glass of which apparatus shall b made. It carries very few recommendations for or against set of several pieces of such apparatus as burners or extractio apparatus.

In the list that follows, D = Discontinue, R = Retain.

…………………

Clamps

(R) Buret, iron, with jaws of pressed steel, japanned and rubber covere
(D) Buret, cast iron.
(D) Buret, polished brass.
(D) Buret, polished brass, nickel plated.

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[1] Presented at the 63rd Meeting of the American Chemical Society Birmingham, Ala., April 3 to 7, 1922

[2] Prepared by the Committee on Guaranteed Reagents and Standar Apparatus of the American Chemical Society in collaboration with th Committee on Standardization of the Association of Scientific Apparatu Makers of the United States of America.

[3] Part I published in THIS JOURNAL, **13** (1921), 1070.

(R) Buret, iron, with strong spring closing the movable jaw

(D) Buret, nickel plated brass, jaws covered with rubber, for attachment to retort stands, etc.

Bunsen, for attaching to supports by fasteners, round jaws, cork lined, with fastener:

Sizes:	Small	Medium	Large
	D	D	D

Bunsen, without fastener, without cork

Sizes:	Small	Medium	Large
	R	D	R

Bunsen, with V-shaped jaws, cork lined, with fastener

Sizes.	Small	Medium	Large
	D	D	D

Bunsen, without fastener, without cork

Sizes	Small	Medium	Large
	R	R	R

(D) **Buret, Allihn, double.**

(R) Buret, double, closing automatically by means of coiled springs; jaws rubber covered.

(R) Buret, Lincoln.

(D) Buret, of wood "Shift Easy."

(R) Buret, Hoffman, double jaws, cork lined

(D) **Buret, double, brass.**

(D) **Townson, for condensers and large tubes; brass, cork lined jaws, 3-in.**

(R) **Universal, for condensers, etc., with swivel jaws; jaws cork lined; without fastener.** (R) **Large size, without fastener.**

(D) **Holdawl, small.**

(D) **Holdawl, large.**

(D) **Holdawl, adjustable form.**

(D) **Ostwald Universal, of brass.**

(D) **Ostwald Universal, double, of brass, with elbow point**

(R) **Fastener, for attaching clamps to rods up to $^{7}/_{16}$ in diameter**

(R) For rods up to $^{9}/_{16}$ in. diameter.

(R) **For attaching clamps to rod at any angle.**

(R) For tubes, nickel plated brass; for screwing into wall, to support tubes, burets, etc.

(R) **Chaddock, spring wire, for holding beakers, size No. 1B, for Beakers Nos. 0 to 2.**

(R) Size No. 3B for Beakers Nos. 2 to 4.

(R) **Chaddock, for evaporating dishes; size No. 3D for dishes 3 to 4 in. diameter.** (R) **Size No. 5D, for dishes 4 to 6 in. diameter.**

(R) **Chaddock, for large test tubes and necks of flasks from $^{1}/_{2}$ to $1^{1}/_{2}$ in. diameter**

(D) **Crucible, brass; for holding crucibles.**

(R) **Test tube, Stoddart, spring wire, nickel plated; for tubes up to 1 in. diameter.** (R) **For tubes $^{1}/_{2}$ to $1^{1}/_{2}$ in. diameter.**

(R) **Test tube, of wood, with wire spring.**

(D) **Test tube, Bunsen, of brass; for tubes up to $^{7}/_{8}$ in. diameter.**

(D) **Wooden, with spring; for large tubes and flask.**

(R) **Apparatus, for holding rods vertical or horizontal on which to clamp apparatus.**

Table, of iron, for fastening apparatus to the table:

Sizes, in.	2	3	4	6	8	10
	D	R	R	R	D	D

Hoffmann, pinchcock, nickel plated; with screw compressor:

Sizes, in.	$^{1}/_{2}$ x $^{3}/_{4}$	$^{3}/_{4}$ x 1
	R	R

(R) **Hoffmann, improved, can be attached to tubing without disconnecting apparatus.**

(D) **Hoffmann, improved, E. & A., superior in quality and workmanship to No. 2078.**

Hoffmann, with one side open:

Sizes:	Small	Large
	R	R

(D) **Bunsen, with screw on each side.**

Mohr, pinchcock, nickel plated, durable:

Sizes:	Small	Medium	Large	Extra Large	Double Extra Large
Length overall, in.	$2^{3}/_{8}$	$2^{7}/_{8}$	$3^{1}/_{2}$	$3^{7}/_{8}$	$4^{5}/_{16}$
	R	R	R	D	D

(D) **Chaddock, pinchcock, of one piece of brass wire, nickel plated.**

Watch glass, brass, nickel plated:

Sizes, in.	2	$2^{1}/_{2}$
	R	R

Watch glass, Bunsen, of brass:

Sizes, in.	2	$2^{1}/_{2}$
	D	D

(D) Condenser, with V-shaped jaws of stamped steel

(R) Tubing, Mohr's pinchcock of *rectangular wire* giving a flat bearing surface on the tubing 3 mm wide. Length, $2^{1}/_{2}$ in. for tubing up to $^{3}/_{8}$ in.

(R) With brass hook for supporting thermometers and other apparatus.

Adjustable, steel.

Maximum opening, in.	6	10	18
	D	D	D

Color Comparison Tubes

(D) Cylinders, Hehner, graduated tubes with stopcocks and metal feet.

Camp, for manganese determination in steel:

Sizes, cc.	30	50	100
	D	D	D

Eggertz, for carbon and manganese in steel, set of two or four:

Capacity, cc.	30	50	100
	R	R	D

Eggertz, with ground-in glass stopper, set of two or four:

Capacity, cc.	30	50	100
	D	D	D

Julian, with bent ends to permit mixing of contents without using a stopper; set of two or four:

Graduated from, cc.	5 to 30	10 to 50	10 to 70
Graduated in, cc.	0.1	0.1	0.5
	R	R	D

Julian, with funnel tops. Per set of two or four:

Graduated from, cc.	5 to 30	10 to 50	10 to 70
Graduated in, cc.	0.1	0.1	0.5
	D	D	D

Nessler, American Public Health Association Standard. Tall form of clear glass, with polished bottoms.

Graduation marks on 50-cc. tubes are from 200 to 250 mm. from the bottom and on the 100-cc. tubes are from 275 to 325 mm. from the bottom. In sets of six or twelve the highest and lowest graduation marks shall not be more than 6 mm. apart.

Jars, Nessler, superior quality, of colorless glass, with polished bottom; selected in sets of two or more agreeing:

Graduated, cc.	50	100	50 & 100	50, 100 & 150
	R	R	R	D

Cylinders

Hydrometer jar, with lip, heavy glass on foot:

Height, in.	4	5	5	5	5	5	6	6	6
Diameter, in.	1	$^{3}/_{4}$	1	$1^{1}/_{4}$	$1^{1}/_{2}$	2	1	$1^{1}/_{2}$	2
	D	D	R	D	D	D	R	R	D
	8	8	10	10	12	12	12	14	14
	$1^{1}/_{2}$	2	$1^{1}/_{2}$	2	$1^{1}/_{2}$	2	3	2	$2^{1}/_{2}$
	R	D	R	D	R	R	D	D	D
	15	15	18	20	20	22	18		
	$1^{1}/_{2}$	2	$2^{1}/_{2}$	2	$2^{1}/_{2}$	3	3		
	D	R	R	D	D	R	D		

Heavy glass ring neck; on foot. D—all sizes:

Height, in.	4	5	6	6	6	7	8	8	8
Diameter, in.	1	2	1	$1^{1}/_{2}$	2	$1^{1}/_{2}$	$1^{1}/_{2}$	$1^{1}/_{4}$	2
	8	10	10	10	12	12	12	12	12
	3	$1^{1}/_{2}$	2	4	$1^{1}/_{2}$	2	$2^{1}/_{2}$	3	4
	15	15	15	16	18	18	20	20	20
	$1^{1}/_{2}$	2	3	2	2	3	2	3	4
	25	25	30	30					
	3	4	3	4					

Hydrometer jars, heavy glass, with flange ground to take glass plate:

Height, in.	6	8	10	12	12	15	15	18
Diameter, in.	$1^{1}/_{2}$	$1^{1}/_{2}$	$1^{1}/_{2}$	2	4	2	3	3
	D	D	R	R	D	R	D	R

Hydrometer jars, with enlarged top:

Height, in.	12	12	14	14	16	16
Diameter, in.	$1^{1}/_{2}$	2	2	$1^{1}/_{2}$	$2^{1}/_{2}$	2
	R	D	R	D	D	R

(R) **Graduated, for Brown-Duvel moisture tester, graduated to 25 cc. in 0.2 cc.**

(R) **Graduated, with enlarged top, for Brown-Duvel moisture tester.**

Drip cup, for acid chamber:

Height of cylinder, in.	5	6	7	10
	D	R	D	D

(D) **Oil sample, flat parallel sides, glass stoppered.** (D) **Graduated 100 cc.**

Filtering, stoneware, acid proof:

Capacity, gal.	$7^{1}/_{2}$	12
	D	D

Graduated, with single graduations:

Capacity, cc.	5	10	15	25	50	100	200	250	300	500	1000	2000	3000	4000
	R	R	D	R	R	R	D	R	D	R	R	R	D	D

Graduated with double graduations, to read up and down. Subdivisions according to the Bureau of Standards:

Capacity, cc.	5	10	25	50	100	200	250	300	500	1000	2000	3000	4000
	R	R	R	R	R	D	R	D	R	R	R	D	D

Graduated in ounces and fractions, single graduations, lipped:

Capacity, oz.	1	2	4	8	16	32
	D	D	D	D	D	D

Graduated and stoppered, single graduations:

Capacity, cc.	5	10	25	50	100	150	200	250	300	500	1000	2000	4000
	D	R	R	R	R	D	D	R	D	R	R	R	D

Graduated and stoppered, double graduations, to read up and down:

Capacity, cc.	5	10	25	50	100	200	250	300	500	1000	2000	4000
	D	R	R	R	R	D	R	D	R	R	R	D

Dishes

Acid, of porcelain:

Diameter, cm.	10	12	13	14.5	16.5
	R	D	D	D	D

Aluminium, flat bottom, straight sides, as used in milk analysis, etc.:

Diameter, mm.	50	65	75	100
	R	R	R	R

(D) Aluminium, flat bottom with slip-in lid.

Crystallizing, flat bottom, straight sides:

Sizes, mm.	50 x 35	60 x 35	70 x 50	75 x 45	80 x 40	90 x 50	100 x 50	115 x 60	125 x 65	150 x 75	170 x 85	190 x 95	215 x 110	250 x 125
	R	R	R	D	R	D	R	D	R	R	D	R	D	R

Evaporating, porcelain, with wooden handle:

Diameter, cm.	12	15.5	21.5
	D	D	D

Evaporating, glass, round bottom, with lip:

Sizes, mm.	50	60	70	80	90	105	125	150	200
	D	D	D	D	D	D	D	D	D

Evaporating, glass, flat bottom, with lip:

Sizes, mm.	50	60	70	80	90	100	125	150	170	200
	D	R	R	R	R	R	R	R	D	R

Shallow, enameled steel:

Diameter, in.	8	10	12	16	18	20	24	28
	D	D	D	D	D	D	D	D

Cast iron, deep, heavy white enameled inside, with detachable handles:

Diameter, in.	7	8	10	13	16	18	22
	D	R	D	D	D	R	D

Lead, round, shallow, for holding hydrofluoric acid:

Diameter, cm.	5	6.5	7.5	10	12.5	15
	R	D	R	R	D	D

Milk, of tin foil, in shape of bottle caps; for milk analysis:

Sizes.	$2^3/_4$ x $^3/_4$	$2^1/_2$ x $1^1/_{16}$	$3^1/_2$ x $^1/_2$
	R	R	R

Solid wrought nickel, round bottom, with lip:

Diameter, cm.	4	5	6	7	8	9	10	12	15
	D	D	R	D	R	D	R	D	D

(D) Solid wrought nickel, for sugar analysis; set of 3.

(R) Nickel, deep form for sugar analysis, diameter 7.5 cm., with large lip and tare weight.

Moisture, aluminium, with cover of same fitting outside:

Diameter, mm.	50	63	90	89	90
Height, mm.	22	44	30	50	15
	R	R	D	R	D

(D) Moisture, aluminium, with dish and cover numbered to agree.

(D) Preparation, of clear white glass, low form, with loose fitting cover.

Opaque fused silica, glazed throughout:

Capacity, cc.	25	45	80	90	100	200	400	500
	D	R	R	D	R	R	D	D

Opaque fused silica, not glazed:

Capacity, cc.	400	500	600	700	800	1200	1400
	D	D	D	D	D	D	D

Capacity, cc.	1800	1800	2500	3000	3000	15000	22500
Diameter, mm.	203	229		311	394		
Depth, mm.	108	89		133	102		
	D	D	D	D	D	D	D

Opaque fused silica, flat, glazed throughout with lip:

Capacity, cc.	20	30	75	150
	D	R	R	D

Opaque fused silica capsule:

Capacity, cc.	10	15	20	30	35	40
	D	R	R	D	R	D

(R) Opaque fused silica capsule for ashing, capacity 40 cc.

(R) Opaque fused silica capsule, large size, capacity 75 cc., diameter 82 mm., depth 25 mm.

Fused silica, incinerating:

Capacity, cc.	7	20
	D	D

Clay, roasting:

Diameter, in.	$2^1/_2$	3	4	5	6
	D	R	R	R	D

Silver, price according to weight:

Diameter, mm.	50	65	75	90	100	125
	R	R	R	R	R	R

(D) Petri-Pasteur, diameter 100 mm., depth of lower dish 7 to 8 mm.

(R) Petri, bottom dish only, diameter 95 mm., depth 12 mm., for use with porous earthenware covers.

(R) Porous earthenware covers, to fit above.

(R) Porous earthenware covers with glazed outer surface.

Petri. Fitted in pairs:

Diameter, mm.	50	75	75	90	100	100	120	120	150	150	200
Height, mm.	10	10	15	10	10	15	15	20	20	25	20
	R	R	D	D	R	R	D	D	R	D	D

"Moist Chamber" with loosely fitting cover with knob:

Diameter, cm.	15	20	25
Height, cm.	4	7.5	9
	R	R	R

(R) Same, without knob on cover.

Slender form with ground grooved cover:

Diameter, mm.	36	50	60	60
Height, mm.	19	26	28	90
	R	R	R	R

(R) Staining, glass, with molded stationary grooves, with cover; for 10 slides, 75 mm. long, width up to 38 mm.

(R) Staining jar, Coplin, for 10 slides.

Extraction Apparatus

Practically all the items discontinued in this section can be made to order without great delay or excessive cost. Very few of them have been bought in the last few years. Recommendations are not made in regard to the kind of glass from which extraction apparatus should be made. For general work it is doubted whether anything more difficult to work than good regular commercial tubing will give enough better service to pay for the greater cost and the frequent lack of neatness of the lamp work. For certain work special glass or even silica may be necessary and sometimes more economical than the regular glass.

Soxhlet, extractor only:

Sizes:	Small	Medium	Large
Approximate diam. inside, mm.	30	38	50
Approx. capacity to top of siphon, cc.	70	100	200
Height of siphon not more than mm.	70	75	113
	R	R	R

Soxhlet, complete with flask and Allihn condenser:

Sizes:	Small	Medium	Large
	R	R	R

(D) Extraction tube—Smalley, for oil.

(R) Extraction tube, of the dimensions required by the Southern Cotton Oil Co.

Soxhlet, with stopcock on side:

Sizes:	Small	Medium	Large
	D	D	D

(D) Extraction tube—Johnson, for fat in milk.

Extraction apparatus, Soxhlet, with two extra flasks, extractor and Allihn condenser; all ground joints:

Sizes:	Small	Medium	Large
Inside diameter, mm.	30	38	50
	R	R	R

Same, with 2 flasks and Graham's spiral condenser:

Sizes:	Small	Medium	Large
Inside diameter, mm.	30	38	50
	D	D	D

Same, with Hopkins condenser, ground joint, and Sy flask for mercury seal:

Sizes:	Small	Medium	Large
	D	R	D

Same, with Knorr flasks:

Sizes:	Small	Medium	Large
	D	R	D

(R) Knorr, with perforated platinum disk.

(D) Same, with perforated glass disk.

(R) Same, flasks supplied with 2 holes in the neck, to take care of return flow of ether.

Parts for above

Condenser (R); flask, 100 cc. (R); extraction tube with platinum disk, loose (R); extraction tube with glass disk (D); extraction tube, *modified form*, with nickel disk and wire clamp or with platinum disk (D)

(R) Knorr, modified by Walter and Goodrich.

(D) According to Prof. G. P. Plaisance.

(R) Bailey-Walker, consisting of glass flask, metal condenser and glass siphon.

(R) Same, with 25-cc. Gooch crucibles in place of glass siphon.

Part for above

Metal condenser (R); glass flasks (R); glass siphon tube (R).

Landsiedl.

Sizes:	Medium	Large
	D	D

(D) *All parts for above*

(R) Extraction tube for fat, Rohrig, Roese-Gottlieb method, ungraduated and unstoppered.

(R) Same, graduated

Extraction apparatus, Bremer:

For solution, cc.	10	25	50
	D	D	D

(D) Graefe.

(D) Hagemann, for liquids.

(D) Kreussler

(D) Cauldwell, tube only with perforated bottom.

Glass tube with siphon.

To siphon, cc.	25	50	100
	D	D	D

Kutscher & Stendel:

Capacity, cc.	500	1000	2000
	D	D	D

Thorn:

Sizes:	Small	Large
	D	D

(R) Wiley.

(R) Parts; glass tube with ground flange.

(D) Wiley, modified by Ford

(R) Wiley, modified by Richardson.

(R) Underwriters' Laboratories pattern.

(R) Same, with suspended porcelain Gooch crucible.

(D) For insoluble test of shellac.

(R) Joint Rubber Insulation Committee form.

(R) Reed, for bark and wood extracts.

(D) Davoll.

(D) Yocum.

(R) Teas.

Extraction shells, alundum:

Height, mm.	90	70	60	80	100	55	127
Diameter, mm.	19	25	26	30	34	35	32
Shape at bottom	Flat	Flat	Round	Flat	Round	Flat	Round
	R	R	R	R	R	R	R

Extraction shells, glass:

Length, mm.	80	80	80	123
Diameter, mm.	25	22	33	43
	D	D	D	D

Filter Paper

Recommendations in regard to filter paper are offered as tentative suggestions for a general stock. It is believed that a number of discontinued items should be obtainable, particularly some of the small sizes. Available records did not show enough sales of the discontinued items to indicate that any great number of chemists desire them.

Unwashed

(D) entire line. Very rapid, for gelatin-like filtrates.

(R) Rapid, suitable for all ordinary work.

Diameter, cm	4.25	5.5	7	9	11	12.5	15	18.5	24
	D	D	R	R	R	R	R	R	R

	27	32	38.5	40	50
	D	D	D	D	D

(R) Sheets.

Slow, for fine precipitates:

Diameter, cm.	4.25	5.5	7	9	11	12.5	15	18.5	24
	D	D	R	R	R	R	R	R	R

	27	32	38.5	40	50
	D	D	D	D	D

(R) Sheets 23 in. x 23 in.

(D) entire line. Very slow, for fine precipitates.

(D) entire line. Extremely slow, for finest precipitates.

Single washed

Rapid, for ordinary precipitates:

Diameter, cm	5.5	7	9	11	12.5	15	18.5
	D	D	R	R	D	D	D

(D) Sheets.

(D) entire line. More rapid, for flocculent precipitates.

Double washed

Used where results are obtained by direct weighing of ignited precipitate.

Very rapid, for flocculent precipitates:

Diameter, cm.	5.5	7	9	11	12.5	15	18.5
	D	D	R	R	R	R	D

Rapid, for ordinary precipitates:

Diameter, cm.	5.5	7	9	11	12.5	15	18.5
	D	R	R	R	R	R	D

Slow, for fine precipitates:

Diameter, cm.	5.5	7	9	11	12.5	15	18.5
	D	R	R	R	R	R	D

(D) entire line. Fat-free, for use in fat determinations.

Extremely low ash content:

Diameter, cm.	5.5	7	9	11	12.5	15
	D	R	R	R	R	R

Hardened

Tough chemically hardened paper for use with filter pumps:

Diameter, cm.	4.25	5.5	7	9	11	12.5	15	18.5	24
	D	D	R	R	R	R	R	R	D

	27	32	38.5	40	50
	D	D	D	D	D

Folded

Folded, strong, high quality, folded in way to prevent tearing at the point:

Diameter, cm.	12.5	15	18.5	24	32	38.5	50
	R	R	R	R	R	R	R

(D) Folded, with parchmentized points.

(D) entire line. Thick folded filters.

(D) entire line. Folded filters of hardened paper.

(D) entire line. Folded filters, for filtration of varnishes, gelatins, and slimy fluid.

(D) entire line. Extra thick, folded filters, very soft and strong.

Extraction Thimbles

Manufacturers of extraction thimbles should give the internal diameter of the same and should not allow a greater variation than 2 mm., the thickness of the wall of the regular thimble should be approximately 1 mm. Discontinuance of the double thickness is recommended.

Retain the following sizes: 19 x 90 mm. 33 x 80 mm
22 x 80 33 x 94 mm.
25 x 80 43 x 123 mm.

(D) entire line. *Black.*
(D) entire line. *Filter Cones.*

Miscellaneous

(D) A strong, rapid paper with low ash.
(D) Arsenic test strips.
(D) Absorption blocks, 14 x 16 mm., purified by acids.
(D) Drop reaction paper, 14 x 22 cm.
(D) Milk analysis strips.
(D) Extra thick, adapted for the filtration of liquors, fruit juices, sirups, and oils
(D) Paper, free from starch.
(D) Soft, for filtration of varnishes, gelatins, etc.
(D) Extra thick. A specially soft and strong filter paper for the rapid filtration of all kinds of varnishes.
(D) Very soft, for rapid filtration of all kinds of varnishes, gelatins, and slimy fluids.
(D) Filter paper in rolls.

Diffusion shells:

Sizes:	16 x 90 mm	35 x 100 mm.
	R	D

(D) Thin diffusion shells, for the determination of free acid in leather.

Funnels

Agateware, with handle:

Diameter, mm.	95	110	140	190	225
	D	R	R	R	R

(D) Agateware, for wide mouth bottles, with handle, 5 in.
(D) Creosote, with stem graduated to 12 cc.

Glass, with angle of approximately 60°, stem ground to a point:

Diameter, mm.	25	40	50	65	75	90	100	125	150	175	200	250	300
Length stem, mm.		50	60	65	75	90	100	125	150		150	150	150
	D	R	R	R	R	R	R	R	R	D	R	R	R

Glass, Bunsen, with exact angle of 60°, with ground rim, long stem:

Diameter, mm.	25	40	50	65	75	90	100	125	150	175	200	225	250	300
Length stem, mm	150	150	150	150	150	150	150	150	150	150	150	150	150	150
	R	R	R	R	R	R	R	D	D	D	D	D	D	D

Glass, Bunsen, with constriction in stem:

Diameter, mm.	50	65	75	90	100
	D	D	D	D	D

(D) Glass, nest of three; one of each $^7/_8$ in., 1 in. and $1^1/_8$ in. diameter.

Glass, without stem, for use in sugar analysis:

Diameter, mm.	75	90	100
	R	R	R

Glass, with bulb in stem:

Diameter, in.	$4^1/_2$	$5^1/_2$	7
	D	D	D

Glass filter, so-called carbon filters, for use with Gooch crucibles:

Diameter, mm. (inside dimensions)	25	28	32	37
	R	R	R	R

Glass, ribbed, for rapid filtering:

Diameter, in.	$2^3/_4$	$3^1/_2$	$3^3/_4$	$4^3/_4$	$5^3/_4$	$7^1/_4$	$8^3/_4$	$10^1/_4$	13
	D	D	R	R	R	R	R	R	R

Glass, ribbed, without stem, for sugar analysis:

Diameter, in.	$2^3/_4$	$3^3/_4$	$4^3/_4$	$5^3/_4$
	D	D	D	D

Glass, with deep conical corrugations for quick filtering:

Diameter, cm.	7	9	16	20	24
	D	D	D	D	D

Alundum, conical filters:

Diameter, in	$1^3/_4$	$2^1/_2$	3	$4^1/_2$
	R	R	R	R

(D) Glass, Spencer, with rubber ring.
(R) Crucible holder, Bailey.
(R) Crucible holder, Walter, for Gooch crucibles of 25 cc capacity.

Crucible holders, Sargent, plain type:

For crucibles top diameter, mm.	27	35	40
	R	R	R

Copper:

Capacity, pts.	$^1/_4$	$^1/_2$	1	2	4	8
	D	D	D	D	D	D

Porcelain, with handle:

Diameter, cm.	8.6	12	17.5
	D	D	D

Porcelain, with small perforations, and handle:

Diameter, cm.	11	13	16	21	26
	D	D	D	D	D

(R) Funnel heater, consisting of 10 coils of copper tubing.
(R) Hot water, Koch's, double wall, inside diameter $5^1/_2$ in.; (D) with single wall.
(D) Hot water, Plantamour's; (D) with steam coil, (D) of polished copper.

Büchner, of acid-proof stoneware:

Diameter, cm.	16	26
	D	D

Hard rubber, polished:

Diameter, in.	$3^1/_4$	$4^1/_4$	$5^1/_8$	$6^1/_8$
	R	R	R	R

Stoneware, acid-proof:

Diameter, in.	4	6	8	10	12	16
	D	D	D	D	D	D

Tin plate:

Capacity, pts.	$^1/_4$	$^1/_2$	1	2	4	8
	D	D	D	D	D	D

(D) Hot water or steam, plain glass, double jacketed.
(D) Same, exhausted and silvered; (D) cover.
(D) Hot air, Lothar Meyer, copper.
(R) Separatory, Carnot's, capacity 200 cc.

Separatory, cylindrical, open top, with glass stopcock, long stem:

Capacity, cc.	30	60	125	250
	D	R	R	D

Cylindrical, glass stoppered:

Capacity, cc.*	30	60	125	250	300	500†	600	1000†	1250
	D	R	R	R	D	R	D	R	D

* Plus 20% Overage.
† The 500-cc. and 1000-cc. sizes to have short stems.

Graduated in cc., cylindrical:

Capacity, cc.	100	125	250	500*	1000*
	D	R	R	R	R

* The 500-cc. and 1000-cc. sizes to have short stems.

Cylindrical, glass stoppered, with side neck:

Capacity, cc.	300	600	1000
	D	D	D

Separatory, funnel shape, 60° angle, heavy glass with stopcock:

Capacity, cc.	125	250	500	1000	2000	4000
Diameter, mm.		100	150	180		
	D	R	R	R	D	D

Separatory, globe shape, light glass, stopper, stopcock and long stem:

Capacity, cc.	30	60	125	250	500	1000	2000
	R	R	R	R	R	R	D

Separatory, globe shape, heavy molded glass, stopper, stopcock, and short stem:

Capacity, cc.	500	1000	2000	4000
	R	R	R	R

Separatory, Squibbs, pear shape:

Capacity, cc.	125	250	500	1000
	R	R	R	D

(R) Separatory, Straus, capacity 30 cc., without stopper.
(R) Separatory, for sulfonation test of creosote, 125 cc.
(R) Separatory, Walter, for delivering single drops, 60 cc.
(D) Shaking, for estimating phenol in creosote.

Thistle top, glass stoppered:

Capacity, cc.	30	60	125	250
	D	D	D	D

Separatory, bell shape, with open top:

Capacity, cc.	30	125
	R	R

(D) C. M. Johnson, globe shape, long stem, open top.

With rod stopper, for quickly separating liquids:

Capacity, cc.	500	1000	2000	4000	8000
	D	D	D	D	D

Stoneware, acid-proof, conical shape:

Diameter, cm.	23	30
	D	D

(D) Sulfur, heavy glass, angle 60°.

Funnel tubes, thistle top, straight:

Length, cm.	20	30	40	45	50
	D	R	R	D	D

Funnel tubes, conical top:

Length, cm.	25	30	40	45	50
	D	R	D	D	D

Safety, thistle top, with bend

Length, cm	30
	R

(D) Safety, conical top, with bend

Safety, with bulbs, thistle top:

No. of bulbs	1	2	3
	R	**R**	**R**

Same, with conical top:

With bulbs	1	2	3
	D	D	D

(D) Vogel, funnel and delivery tube, combined.

Funnel tube, heavy, short stemmed with bend and two bulbs for use with **gas generator:**

Sizes:	Small	Large
	D	R

(To be concluded)

Chemical Engineering Education Conference

At the conference on Chemical Engineering Education, conducted by the American Institute of Chemical Engineers at Brooklyn Polytechnic Institute on May 16, the following recommendations were finally adopted:

1—An undesirable multiplicity of subjects is now included in courses in chemical engineering.

2—Wherever possible, it is desirable to avoid splitting major courses into a number of minor courses.

3—Any course in chemical engineering should provide, as the background for specific instruction in chemical engineering as such, strong courses in chemistry, physics, mathematics, and the fundamentals of engineering.

4—As preliminary to the desirable reorganization of chemical engineering courses, steps should be taken to secure agreement on the nomenclature concerned with the subjects involved.

5—A much closer agreement in the weighting of the various courses as to clock and credit hours is urgently needed in those institutions giving courses in chemical engineering.

6—The committee would omit from chemical engineering curricula courses in civil engineering, sanitary engineering, mining engineering (except geology), and electrical engineering beyond its fundamentals, which should include the instruction required for the erection and operation of motors and generators.

7—It is desirable to avoid specialization by industries in the four-year course in chemical engineering. When specialized training is offered, the specialized subjects should preferably be segregated as graduate work. This applies to such subjects as petroleum technology, sugar, cellulose technology, fuels and oils, and refrigeration.

8—The committee considers a thorough grounding in English, a reading knowledge of some foreign language, and a reasonable familiarity with English literature essential to the adequate training of the chemical engineer, and regards English as one of his most effective working tools. It recommends a special course in report writing and the oral presentation of projects.

9—The committee recommends that a "source of information" course or its equivalent be provided as a part of the chemical engineering course. This specialized course should familiarize the student with patent literature, governmental reports, bibliographies, trade journals and catalogs, abstract journals, publications of societies and other technical literature, the resources of libraries, and the activities of scientific and technical organizations throughout the world.

10—The committee recommends that, wherever possible, engineering studies should be preceded by three years of general college training, in which special emphasis be given to mathematics, physics, chemistry, English history, and economics, with the idea of obtaining a broad foundation for their professional study and of entering upon this study at a greater maturity and with presumable reduction of time required for their professional courses.

11—The committee wishes to emphasize the fact that the chemical engineering profession is a difficult one and that, accordingly, a thorough and broad preparation for entrance should be insisted upon by institutions offering courses in chemical engineering.

12—The committee recommends that technical schools and professional schools of universities arrange their courses so that properly qualified college graduates may secure a professional degree at the end of a two-year course.

13—The committee deprecates the use of undergraduate or even graduate students as major instructors (instructors of laboratory sections or quiz sections) in charge of classes of chemical engineers, even in the freshman year.

American Oil Chemists' Society

THE American Oil Chemists' Society held its thirteenth annual convention at the Grunewald Hotel, New Orleans, La., on June 7 and 8, 1922. On account of conditions prevailing in the Mississippi Valley early in May, the meeting was postponed from May 8 and 9 until this time. What was lacking in attendance owing to the postponed date and the general financial condition in the vegetable oil industry was more than compensated for by the enthusiasm of those present.

Edmonston Washington, D. C.

L. M. Tolman,
President, American Oil Chemists' Society

The committee reports were printed and distributed at the meetings, as was done last year. This plan permits those present to give these reports more consideration than if the papers were merely read, brings out the more important features of the reports for discussion, expedites the disposal of the reports, and leaves ample time for the consideration of other more important papers.

Dr. Geo. S. Jamieson, Chemist in Charge of the Oil, Fat, and Wax Laboratory of the U. S. Bureau of Chemistry, and an Honorary Member of the Society, presented a most important paper as the result of his laboratory's investigations on the composition of vegetable oils, with particular reference to cottonseed oil, under the title of "The Analysis of Crude Vegetable Oils." Dr. Jamieson outlined a method for the determination of the actual amount of pure glycerol in crude vegetable oils. His investigations have also revealed that in the usual refining processes of cottonseed oil other substances than the free fatty acids combine with the caustic soda used. He has isolated a small quantity of these substances and has found them to contain phosphorus and other inorganic radicals. When the values of these non-fat bodies have been determined and the part that they play in actual commercial refining operations is known, it will be much easier than at the present time to judge the efficiency of the refining operations.

Dr. David Wesson, Technical Director of the Southern Cotton Oil Co., and one of the founders of the American Oil Chemists' Society, had his new E. K. Colorimeter on exhibition at the meeting. With this instrument Dr. Wesson has been making an exhaustive study of the possible solution of the various difficulties surrounding the present color grading of vegetable oils. He also described and showed lantern slides of another instrument which is being perfected by Keuffel & Esser Co., showing a number of oil absorption curves of oils and Lovibond glasses. An interesting feature in regard to this was that the curves for refined cottonseed oils show at one point a striking depression which may be nearly eliminated by bleaching with fuller's earth. Dr. Wesson said that with the Keuffel & Esser instrument it will be possible to tell whether a given oil has been partly bleached or whether a given refined oil is bleachable.

Suitable resolutions were presented as memorials to Dr. Frank N. Smalley and Dr. Charles Baskerville, both members of the Society claimed by death during the past year. As a further memorial to Dr. Smalley, the Society's coöperative analytical program of work on cottonseed meal is to be known as the Smalley Foundation.

A number of certificates of proficiency in analytical work, as a part of the coöperative analytical program, were given to several of the members by Herbert Bailey, Chief Chemist of the Southern Cotton Oil Co., and chairman of the committee on this work. The subjects covered by this program this year were meals (for ammonia and oil), oils, soapstocks, fats, and fertilizers.

The Society's silver loving cup, which is presented each year to the member doing the most accurate work on its set of coöperative meal samples, was awarded at the annual banquet to Dr. H. B. Battle of Montgomery, Ala. This work consisted of thirty-eight meal samples during the year, on which there were nearly one hundred collaborators.

The report of the Secretary-Treasurer showed the Society to be in an excellent financial condition, and that, notwithstanding the business depression that has existed and the large number of members lost, there has been a growth of 15 per cent in its membership.

The Society voted, upon recommendation of its Governing Committee, to incorporate under the laws of Louisiana.

The following officers were elected for the ensuing year:

President: L. M. TOLMAN, Chief Chemist, Wilson & Co., Chicago, Ill.

Vice President: H. B. BATTLE, The Battle Laboratory, Montgomery, Ala.

Secretary-Treasurer: THOS. B. CALDWELL, Manager, Law & Co., Wilmington, N. C.

Editor Chemists' Section: HERBERT BAILEY, Chief Chemist, Southern Cotton Oil Co., Savannah, Ga.

THOS. B. CALDWELL, *Secretary*

LONDON LETTER

By STEPHEN MIALL, 157 Haverstock Hill, Hampstead, N. W. 3, England

The success of a chemical works largely depends on its efficiency, and it is not surprising that the chemical engineers, who consider that the prosperity of the world will be a function —in expanding terms—of the efficiency of industrial chemistry, take themselves somewhat seriously. Great debate has taken place on the relative importance of engineering and chemistry, how best to combine the two. About three years ago, the radioactive chemical engineers in this country formed a separate group of the Society of Chemical Industry. It is characteristic of all radioactive bodies to maintain a temperature rather above the normal. The greater the effusion of energy, the greater is the bombardment of neighboring bodies, but in due course a state of equilibrium is reached. It seems probable that this state has now been attained in this country; the Chemical Engineering Group has published and is continuing to publish very valuable reports on filtration and on a variety of other subjects, and at the next annual meeting of the Society of Chemical Industry, to be held in Glasgow in July, there will be papers contributed by members of the Group on the design of ammoniacal liquor stills, on tar distillation, and on other matters connected with distillation. The chemical engineers are also organizing an Institute of Chemical Engineers which, in comparison with the Group, will consist of the same atoms only slightly differently arranged.

PAINT AND VARNISH INDUSTRY

There are always two opposing forces at work in bodies of scientific men, a tendency toward fission and a tendency toward fusion. Attraction and repulsion prevail in turn, just as individualism and communism are fashionable in their respective seasons. An effort is now being made for a fusion of the scientific societies concerned in the paint and varnish industry, and if the effort succeeds it is hoped that the dissemination of scientific knowledge in this domain will be better done than has hitherto been possible here.

SLOWLY IMPROVING CONDITIONS

Trade conditions seem a little better; the income tax has been reduced by a shilling in the pound, and that is something at any rate. The heavy chemical trade here is appreciably better than it was, and the home demand for products of other trades is improving, but, generally speaking, the export trade has hardly enough vitality to keep it from putrefaction. Unfortunately, there is only one remedy for this trouble and it is slow in its operation. We and you and all other countries will have to live laborious days, deny ourselves a lot of luxuries we are, or have been, accustomed to, write down in our balance sheets the capital values of our works and our plant, effect economies in our process costs, and so gradually put all our concerns into a sound and prosperous state so that the world can again become rich enough to indulge in that international trade on which so many of us depended for our butter—bread we can sometimes procure out of our home trade.

INTERNATIONAL CONFERENCES

This is the season for international conferences. One has recently been held in Brussels and a number of very interesting papers were read, including one on "Molecular Configuration and Optical Activity," by Sir William Pope, one on "X-Ray Analysis and Molecular Structure," by Sir William Bragg, and one on "The Separation of Isotopes," by Messrs. Perrin and Urbain. No one thought a few years ago that the researches of Sir William Crookes on the rare earths would prove to be an important stage in the development of the gas mantle industry, or that the work of Pictet, Cailletet, Dewar, and others on the liquefaction of gas would effect a revolution in industrial chemistry. It may be that in future years the theoretical work on the nature of the elements and their relationship to each other will have results which no one can at present foresee.

Then we are to have the annual meeting of the Union Internationale de la Chimie Pure et Appliquée at Lyons at the end of June. The British delegation will probably include Sir William Pope, Professors Lowry and Soddy, Dr. Aston, and the writer.

I hear that the Jefferies-Norton system for the production of oxygen on the large scale is attracting attention over here; this process, which I fancy hails from Massachusetts, has been described in many papers published in American journals, and it is quite on the cards that it will provide oxygen in bulk at a less cost than any previous process. I hear from more than one source that its possibilities seem very interesting, and that installations of the plant are under consideration.

The Low Temperature Carbonization Company report that their plant at Barnsley in Yorkshire is working smoothly and that interesting developments will be published shortly.

Dr. E. F. Armstrong is nominated as the new president of the Society of Chemical Industry and will no doubt act with his characteristic energy. The Society has a number of intricate and important matters of policy to consider during the next two or three years, and one of the most difficult is how best to achieve some such coördination of chemical interests as you have successfully accomplished in America.

May 15, 1922

Continuance of the qualified embargo of foreign dyes was endorsed by the American Cotton Manufacturers' Association at its annual convention held in Washington, D. C., recently.

WASHINGTON NOTES

The Tariff

Notwithstanding the numerous vehement attacks made against the domestic dye industry by Senator King, the Senate has passed Paragraphs 25 and 26 relating to dyes. Paragraph 25 carries a duty of 50 per cent ad valorem and 7 cents per pound on crude coal-tar dyes, and Paragraph 26, 60 per cent ad valorem and 7 cents per pound on intermediates. The dye embargo, around which the greatest opposition centers, has been passed over temporarily, but it is generally conceded that the tactics employed by the opposition to prevent its passage will, in reality, be a blessing in disguise to the industry, and while the fight will be a long and bitter one it seems certain that sufficient votes will be secured to guarantee the retention of the embargo clause in the bill.

With one or two notable exceptions, the Senate has stood strongly back of the recommendations of its Finance Committee. It overruled the committee, however, when it placed cyanide and manganese on the free list.

It is greatly to be regretted that the Senate changed the duty on scientific and laboratory instruments and apparatus from 55 to 35 per cent, and it is to be hoped that the conferees will restore the 55 per cent duty when the bill goes to them for consideration.

Muscle Shoals

The House Committee on Military Affairs, after exhaustive hearings covering several months, has introduced a bill in Congress recommending that the Ford offer, as modified by the committee and approved by Mr. Ford, be accepted with the single exception that the Gorgas Warrior steam plant be eliminated from the proposal. In submitting its report the committee urged upon Congress the desirability of early action in accepting the Ford proposal and in the enactment of the necessary legislation. Minority members of the committee have also introduced a bill recommending that the Ford proposal be accepted in its entirety. Still other members of the group feel that the Ford proposal should undergo further modifications before it is accepted, and have so recommended to Congress. Meantime, the Attorney General has decided that the contracts entered into by the War Department and the Alabama Power Company, which were believed by some to give the Alabama Power Company exclusive or preferential rights to purchase the Gorgas plant and Nitrate Plant No. 2, are invalid.

The Senate Committee on Agriculture and Forestry has practically concluded the hearings which it has been conducting for some weeks on Muscle Shoals, although upon request it continues to hear witnesses from time to time. Senator Norris, Chairman of the committee, has introduced a bill in the Senate providing for the operation of the Muscle Shoals project by a government corporation to be known as the Federal Chemical Corporation, and the Senate has passed an amendment to the Army Bill appropriating $7,500,000 to continue the work on the Wilson Dam. Just what action will be taken by the conferees upon this amendment remains to be seen. Much interest centers around this action, particularly in view of the increasing sentiment among representatives in favor of the acceptance of the Ford proposition in an amended form as recommended by the Committee on Military Affairs.

Reparation Dyes

On June 16 Senator Shortridge introduced the following Joint Resolution which was referred to the Committee on Foreign Relations:

> *Resolved* by the Senate and House of Representatives of the United States of America in Congress assembled that the President be and he is hereby authorized and requested to take such measures as may be required to secure for the United States of America or its Nationals the dyestuffs and chemical drugs to which the United States of America may be entitled under Section 1, Article 2 of the Treaty of Peace between the United States of America and Germany, proclaimed November 14, 1921.

The appointment of C. R. DeLong as head of the new Chemical Division of the Bureau of Foreign and Domestic Commerce is announced. Mr. DeLong is at present head of the Chemical Section of the Tariff Commission and will assume his new duties in the Department of Commerce on August 1.

A Boost for Chemical Warfare Service

The Senate amended the Army Bill by increasing the appropriation for Chemical Warfare Service from $500,000 to $750,000. One million dollars was originally requested as the minimum amount necessary for the efficient conduct of this work. If the conferees agree to this amendment, therefore, it will mean that Chemical Warfare Service will be able to preserve more of the nucleus of its organization, which is imperative if it is to carry out a well-rounded program of research and development.

Conservation of Helium Gas

The bill before Congress authorizing the conservation, production, and exploitation of helium gas has for its main object the conservation of our fast-diminishing supply of helium gas. At the present time it is estimated that 500,000,000 cu. ft. of helium gas are lost annually through the ordinary commercial use of natural gas containing it. The bill carries with it an appropriation of $5,000,000, of which $4,000,000 are desired for conservation purposes and $1,000,000 for the purchase or control of gas fields, drilling wells, laying of pipe lines, and for the construction of a plant on or adjacent to the contemplated gas fields purchased, for the purpose of supplying such amounts of the gas as may be necessary to meet the future requirements of the Army and Navy. The bill was considered in conference by the Secretaries of War, Navy, and Interior and has been unqualifiedly approved by them. It has also been strongly endorsed by the President. If the bill is passed in its present form it will put all work of extracting helium from natural gas under the Interior Department.

Dr. R. B. Moore, Chief Chemist of the Bureau of Mines, gave a public lecture at University College, London, on May 24, 1922. He chose for his subject "The Commercial Manufacture of Helium by the Government of the United States."

Dr. Richard C. Tolman has resigned as Director of the Fixed Nitrogen Research Laboratory to accept a position as Professor of Physical Chemistry and Mathematical Physics in the Departments of Chemistry and Physics at the California Institute of Technology, Pasadena, Cal. The California Institute of Technology has recently been reorganized with Prof. R. A. Millikan as Director of the Norman Bridge Laboratory of Physics, and Prof. A. A. Noyes as Director of the Gates Chemical Laboratory. The Institute plans a strict limitation on the number of undergraduate students, and will concentrate on graduate and research work. An active coöperation will be maintained between the research work of the Institute and that of the Mt. Wilson Solar Observatory along the fundamental lines of common interest to physics, chemistry, and astronomy.

Dr. Tolman will assume his new duties at the commencement of the fall term.

Dr. F. G. Cottrell has been appointed to succeed Dr. Tolman as Director of the Fixed Nitrogen Research Laboratory.

At the meeting of the Trustees and Editorial Board for the publication of Critical Tables of Physical and Chemical Constants which was held in Cleveland, May 21, 1922, it was agreed that the official designation of the tables should be "International Critical Tables;" the sub-title to read "Tables of Constants and Numerical Data of Physics, Chemistry, and Technology Critically Prepared under the Auspices of the International Research Council."

It was decided that the initial office staff should consist of an editor, one chemist, one physicist, and such other assistants as should be needed during the progress of the work. Dr. C. J. West was appointed as the assistant editor representing chemistry. The editor was authorized to arrange for one corresponding member of the editorial board for each country represented in the International Research Council, and to visit certain European experts for the purpose of securing their coöperation and assistance in the compilation of the Tables.

Dr. John Bassett Moore has been appointed to represent the United States on the Rules of Warfare Commission, authorized by the Disarmament Conference. The Commission will consist of not more than two representatives from each of the following countries: United States, Great Britain, France, Italy, and Japan.

June 17, 1922

PARIS LETTER

By Charles Lormand, 4 Avenue de l'Observatoire, Paris, France

Information which we receive from the United States indicates the approach of the end of the economic crisis which has been felt in America as well as in France. We learn, for example, that the steel industry is working at 85 per cent capacity and that the number of workmen has had to be increased. These are encouraging indications and console us a little for vain and profitless political conferences.

Petroleum and Other Fuels

The general opinion that the Genoa Conference was essentially a petroleum conference has aroused in France an inclination to try to economize as much as possible in the precious product.

The different borings in Auvergne to which I have referred this past year have unfortunately not yet given results. They are being persistently investigated, and sometimes gas and a little oil are found, sometimes nothing. These alternations of success and failure are bound to be discouraging, but the engineers are persisting in their researches.

I have also spoken of various organizations, such as on a national motor fuel, and the committees on the carbonization of coal and lignite. These organizations are seeking, each in its own sphere, for the better utilization of the distillation products of coal and of lignite. This will also be true of the congress on petroleum, or rather on combustible liquids, which is to be held in France in October.

One of the combustibles already studied is the hydride of naphthalene. This product, under the name of tetraline, was made in large quantities by the Germans during the war, who used it in mixture with alcohol and benzene. It is obtained by the catalytic hydrogenation of naphthalene.

Except at some large gas works, naphthalene is not recovered in France. The plan would be to instal in all the small gas works apparatus for the total recovery of by-products, even in factories with a capacity of 1,000,000 cubic meters per year, which is very low. The naphthalene thus recovered and collected would finally be hydrogenated with hydrogen obtained by the Haber process. The hydrogen apparatus developed and installed would serve, later, as a type for the installations intended for the fixation of nitrogen.

It is of interest to settle definitely the cost of hydrogen by the Haber and Claude processes. Discussions of this question are far from settled. According to Mr. Lheure, Director of the Claude factory, the price of hydrogen by the Claude process would give an economy of 16 per cent over the Haber process. The price of hydrogen would be 2 fr. 45 per 100 cubic meters. On the other hand, according to Mr. Patard, Director General of Explosives, it would be necessary that the hydrogen be sold at a very low price, about 8 fr. 64 per ton of fixed nitrogen, or 0 fr. 33 per 100 cubic meters. According to Mr. Patard, the Claude process involves a selling price of hydrogen higher by 40 per cent than that used at Oppau.

Baryta in the Sugar Industry

Also in the field of industrial chemistry, Mr. Baud has found an ingenious solution of the use of baryta in the sugar industry. It is known that extraction of sugar as barium sucrate is much more satisfactory in yield than extraction with lime. Fifteen per cent of the sugar produced is in the molasses and cannot be recovered with lime, while with baryta this is possible. The objection to the baryta extraction lies in the fact that barium carbonate requires a temperature of 1500° for conversion to baryta, and the furnaces used for calcination are rapidly destroyed on account of the alkalinity of the product.

Mr. Baud has shown that one can advantageously use tribarium silicate, $SiO_2.BaO + BaCO_3$. This silicate regenerates its baryta easily at 1280° and the walls of the furnace are not attacked.

Washing on a Small Scale

Mr. Lumière, of Lyons, has been making a study of industrial washing, and has obtained very interesting results. Using a little siphon consisting of a twisted strip of cotton, he has completely washed a 9 × 12 photographic plate with 30 cc. of water in 12 to 15 minutes.

The method used is most ingenious, and makes possible not only the washing of photographic plates with very small amounts of water in a very short time, but also the washing of precipitates and the separation of liquids from suspended materials.

The process is susceptible of great industrial application.

Studies on Sea Water

Up to this time people have believed that, while saline concentration in sea water might vary, the ratio of the elements contained therein was always the same. By taking the density of sea water and consulting the Knudsen tables, the degree of salinity was easily obtained.

Messrs. Gabriel Bertrand and Frendeler have demonstrated that the ratio of the different elements is not as constant as has been assumed. They have studied especially the variations in calcium and magnesium at different points. Other investigations along the same lines have been made, and their conclusions will be reported at the International Conference at Lyons at the end of this month.

The samples of standardized sea water furnished by Denmark would no longer be used as a basis of comparison. One would simply make halogen determinations.

Pure Scandium Salts

Mr. Georges Urbain, a member of the International Committee on Atomic Weights, is continuing his excellent work on the rare metals.

He has been able to prepare very pure samples of scandium salt, starting from the mineral thorveitite and using potassium sulfate. This will make possible the pursuit of work on this little known element.

With one of his collaborators, Mr. Dauvillier, Mr. Urbain has also been able, by means of high frequency spectra, to determine exactly the atomic numbers of the new elements which he has discovered.

In 1914 Mr. Urbain followed the experiments of Moseley. The death of the latter during the war interrupted his work.

The conclusion of Mr. Urbain's work is that the ytterbium of Marignac contained three elements: neoytterbium, with atomic weight 70, lutecium, with atomic weight 71, and celtium, with atomic weight 72. The use of high frequency spectra has, alone, made possible this separation.

Mother of Pearl

Messrs. Clement and Rivière have shown that the nacre, very common in shells, is due to a network phenomenon, which can be very simply reproduced by pouring on the surface of gelatin containing a calcium salt a solution of sodium carbonate and sodium nitrate. There forms at the interface of the gelatin and the liquid calcium carbonate, in a network of fibers absolutely identical, from the optical point of view, with nacre.

The International Conference at Lyons opens June 27, and will be followed by the Congress of Industrial Chemistry at Marseilles. I shall attend these meetings and will not fail to report the interesting points.

June 2, 1922

Lead Pigments

The following table shows the quantity and value of lead pigments marketed in the United States in 1920 and 1921, as reported by producers to the United States Geological Survey.

	1920			1921		
		Value			Value	
	Short Tons	Total	Per Ton	Short Tons	Total	Per Ton
Sublimed lead[1]						
White......	12,412	$2,083,647	$167.87	11,568	$1,418,403	$122.61
Blue ...	928	153,657	165.58	463	58,593	126.55
Red lead.....	34,431	7,523,089	218.50	21,814	3,410,904	156.36
Orange mineral				379	91,184	240.59
Litharge.....	62,329	12,386,185	198.72	41,953	5,740,690	136.84
White lead:						
Dry.......	33,678	6,351,798	188.60	26,695	3,749,851	140.47
In oil......	112,017	25,986,100	231.98	143,634	27,713,257	192.94

[1] Includes basic sulfate lead.

Personals

The recent death of the Swiss chemists **Phillipe A. Guye** and **Traugott Sandmeyer** will prove a great loss to chemistry. In addition to his important work in organic and physical chemistry and in the determination of atomic weights, Guye founded the *Journal de Chimie Physique* and was active in founding the *Helvetica Chimica Acta*. He was a member of the International Committee on Atomic Weights, honorary member of the Royal Society and of the chemical societies of Madrid, London, Petrograd, and Bucharest, a Chevalier de la Légion d'Honneur, and recipient of the Prix Vaillant and the Davy Medal. His death occurred in his sixtieth year.

Sandmeyer's eminent work was in the field of dyes, in which he made many remarkable discoveries. Among his achievements were the discovery of diamidophenyltolyl, of the process for making auramine, of the method for producing dyes of the triphenylmethane class, of the preparation of indigotin from thiocarbanilide, and a new method for manufacturing isatins. For more than thirty years he was a member of the firm of J. R. Geigy & Company.

Ernest Solvay, inventor of the Solvay process for the manufacture of soda, died at Brussels, Belgium, on May 26, 1922, in his eighty-fifth year. Solvay was the son of a salt refiner of modest means and had great difficulty in bringing through to commercial success the invention which finally made him one of Belgium's richest men. He received many honors, among them the Lavoisier Medal of the Institute of France, the Grand Medal of the University of Paris, and the appointment as a Grand Officer of the Order of Leopold. On his seventy-sixth birthday he presented $100,000 each to the Universities of Paris and Nancy and divided $1,000,000 among Belgian educational and charitable institutions and the employees of his firm, the Solvay Society of Brussels. On May 27, 1920, he was presented by the American Ambassador with a certificate of honorary membership in the AMERICAN CHEMICAL SOCIETY.

Mr. V. L. Nickle has left The Western Cartridge Co., East Alton, Ill., and has accepted a position with the J. P. Devine Co., Buffalo, N. Y.

Dr. L. V. Burton has left the employ of the Illinois Canners Association, where he has been doing research on methods of grading canned corn, to go to Libby, McNeill & Libby, Chicago, Ill.

Mr. Edgar S. Ross, formerly chief chemist for the Charlotte Chemical Laboratories and Columbite Reduction Company of Charlotte, N. C., and for the past several years engaged in private research concerning the metals tantalum and columbium, is now chemist and assistant manager for McKechnie Brothers, Inc., metal smelters and refiners, Philadelphia, Pa.

Mr. S. M. Kintner has been recently appointed manager of the research department of the Westinghouse Electric and Manufacturing Company to succeed Mr. C. E. Skinner, who is now assistant director of engineering.

Mr. Fletcher C. Benton, formerly connected with the Ohio Fuel Supply Co., Utica, Ohio, as research chemist working on the synthesis of formic aldehyde from natural gas, is now in the physical chemical section of the Bureau of Mines, Pittsburgh, Pa., assisting in the research on the activation of several seams of representative soft coal.

Dr. T. F. Aschman of Pittsburgh, Pa., chemist to the Pennsylvania Bureau of Foods, has been elected chairman of the Board of Chemists of the Bureau, to succeed the late Dr. William Frear.

Mr. Hugh M. Henton, formerly instructor in metallurgy at Case School of Applied Science, has opened an office as consulting engineer in the National City Building, Cleveland, Ohio.

Mr. C. H. Kidwell, formerly with the Semet-Solvay Co., Syracuse, N. Y., is now with Dr. Raymond F. Bacon, who has recently opened a consulting chemical engineering practice at 50 E. 41st St., New York City.

Mr. Leslie B. Coombs has resigned his position with the Atlantic Dyestuff Co., Boston, Mass., to become superintendent of the Victory Products, Inc., Westboro, Mass., manufacturers of paints and kindred specialties.

Dr. Colin G. Fink has been appointed Lecturer in Electrochemistry and will have charge of that division of the Department of Chemical Engineering, Columbia University, beginning July 1. He will continue his services as secretary of the American Electrochemical Society, office facilities having been arranged at Columbia for this.

Industrials

Verdict in favor of the American Trona Corporation has been rendered in the case of the Hubbard Fertilizer Company against the corporation for alleged loss through using potash furnished by the Trona Corporation. The Hubbard Company claimed that potash purchased in 1918 contained borax in excess of the contract specifications, and sued for $275,000, but it was decided by the court that no breach of contract had been shown.

During the month of May twenty firms were organized to engage in the manufacture and distribution of chemicals, drugs, and dyes, with an aggregate indicated investment of $3,671,000 as compared with $20,055,000 in April, and $12,625,000 in March.

The Carnegie Steel Company is to build at Clairton, Pa., another by-product coke plant to cost from $30,000,000 to $35,000,000, which will have a capacity more than double that of the present plant. The new plant will have fourteen batteries of ovens, which will cover 65 acres of ground and require 30,000 tons of coal per day to charge them all.

The Textile Alliance has issued *Bulletin* **40** which lists a wide variety of German dyes available for delivery on receipt of the necessary permit. Prices are quoted for dyes in original containers, f. o. b. warehouse, Long Island City, but the quantities of dyes available are not given.

By a decision of the court in the action of the General Bakelite Company against the General Insulate Company, the validity of the Baekeland patents is confirmed. The action, which charged infringement in the use of redmanol, was defended by the Redmanol Chemical Products Company. Announcement has since been made of a merger of the General Bakelite Co., the Condensite Company of America, and the Redmanol Chemical Products Co., as the Bakelite Corporation. The three companies will continue separately to manufacture and market their products. As a result of the merger new development and research work is already under way.

The Buffalo Foundry & Machine Company has recently acquired the coppersmithing business of the W. A. Case & Son Mfg. Co., of Buffalo, including the copper shop equipment, and the company is now in position to furnish all kinds of copper work, including distilling apparatus, evaporators, kettles, vacuum pans, coils, etc., and to do a general coppersmithing business either in new work or repairs.

In a compilation made for the Finance Committee of the Senate by the Bureau of the Census, it is shown that there are 598 establishments in the United States engaged in the manufacture of chemicals. The capital employed is given as $484,488,412, salary and wage payments as $97,188,958, and the value of the products in 1919 as $438,658,869. The average number of wage earners employed during 1919 was 55,586. The establishments pay $28,338,749 in federal taxes and $3,592,640 in state taxes.

An explosion occurred in the new Haber process plant of the Atmospheric Nitrogen Corporation at Solvay, N. Y., on June 11, in which four persons were injured. Officials were not able to explain the cause of the accident or to estimate the damage, which was confined to the interior of the process building. Repairs were immediately started in order to permit normal operation as soon as possible.

At the May meeting of the National Council of Dyes and Colors, recommendations regarding the tests which colors must be able to withstand to assure dye fastness in goods were submitted by W. M. Scott of Cheney Brothers, and it was decided to submit the recommendations to the various industries for opinions on their practical value.

The Cooper-Hewitt Electric Company has made available for the first time a small high intensity arc of the mercury vapor type in quartz and has published a bulletin describing the various laboratory uses of the arc.

The National Exposition of Power and Mechanical Engineering is to be held at the Grand Central Palace, New York City, December 7 to 13, inclusive, immediately following the annual meeting of the American Society of Mechanical Engineers. It is expected that the exhibits will supplement the program and discussions of the Society, which will hold sessions relating to fuels, stokers, steam power plants, railroad, steam utilization in the paper industry, textile and gas power.

BOOK REVIEWS

Potash. By Sydney J. Johnstone, B.Sc. (London), A. I. C. Scientific and Technical Department, Imperial Institute. Monographs on Mineral Resources. 122 pp. John Murray, Albemarle, St., W., London, 1922. Price, 6s. net.

The widespread interest in potash makes this work especially valuable for reference purposes.

The chapters of greatest interest as bearing on the potash situation in this country are the second, third, seventh, eighth, and tenth.

In the second chapter the usual emphasis is given to the idea that in the formation of the earth's crust the Creator so arranged things that the rock salt formed by the desiccation of inland seas included enormous deposits of potash salts in Germany, considerably less extensive ones in Alsace, and a number of scattering traces in the other countries mentioned, with none at all in the United States.

No mention is made of the probability that the very intensive and extensive search made in Germany, aided by the knowledge gained from hundreds of years of salt mining there, accounts for the apparent Providential favor and that an equally extensive and intensive search of the enormous salt fields of the United States would be likely to develop equally great deposits of potash here.

Chapter three gives very interesting information regarding the possibilities from alkaline lakes and depressions particularly in the western United States, from where our most quickly produced potash output came during the war.

Chapter seven touches on some twenty-five main processes, many of them typical of many others that have been developed more or less successfully, mostly in the United States, for recovering potash from the silicates and other insoluble potash-bearing rocks. All of these depend for success on the profitable disposal of by-products. A careful reading of this chapter with reference to suitable marketing arrangements for the by-products, most of which are staple commodities used in enormous tonnages, shows that here is the basis for a large output of potash in many parts of the United States and that when quantity production is developed costs will evidently be far below anything so far possible. More than in any other phase of potash development in the world, is here shown the fecundity of the chemist in devising the means to get "bread out of stone." Those who have been so prone to attribute inferiority to American chemists will here have opportunity to revise their opinions.

Chapter eight shows the enormous amounts of potash recoverable from the flues of the portland cement and blast furnace industries. It would appear that, properly collected, the potash from these two sources alone is capable of supplying more than the 250,000 tons of K_2O per annum imported by the United States in 1913.

Chapters nine, ten, and eleven show the importance of vegetable waste, sugar refining and alcohol distillery wastes, and wool washing wastes as sources of potash supply. One impressive piece of information is that banana skins contain over eleven per cent of potash.

The list of references at the end forms a most valuable compendium of the principal potash literature of the world.

On the whole, the conclusions and remarks give the general impression that the world in general and the United States in particular must turn perforce to Germany for about seventy-five per cent and to Alsace for about twenty-five per cent of its supply of potash at cheapest prices. If thoroughly studied and dissected beyond and behind these conclusions, however, this book will serve the chemist and engineer as a splendid source of facts and arguments to prove that, with reasonable opportunity to secure permanently and properly invested capital, the United States is in a magnificent position to develop not only its own entire present and enormous prospective needs of potash, but to do its part for the rest of the world, in dissipating Germany's control of this important substance.

H. D. Ruhm

Aluminium and Its Alloys. Their Properties, Thermal Treatment, and Industrial Application. By C. Grard, translated by C. M. Phillips and H. W. L. Phillips. 184 pp. D. Van Nostrand and Co., New York, 1922. Price, $5.00.

This book is a translation of the French edition of Colonel Grard's book "L'aluminium et ses alliages," Berger-Levrault Paris, 1920, and is the American edition of the same work brought out in England in 1921, by Constable and Co., Ltd. The author is well known as an ordnance engineer and for his work in the heat treatment of worked nonferrous metals and is well qualified to present the subject in a clear form, but this neither he nor the translators have done.

The book is largely a collection of test data relating to the physical properties of worked and heat treated aluminium, cast light aluminium alloys, and worked and heat treated alloys of the duralumin type and of aluminium bronzes. Collected by Colonel Grard during the late war in connection with the production of aircraft in France, the test data in themselves are exceedingly valuable, but the arrangement and make-up of the book are exceptionally bad—in fact the worst that have come to the attention of the reviewer in some time. From an editorial point of view the work is almost everything that it should not be, while, technically, there are a number of errors, and details of methods used in carrying out the tests are lacking.

The work treats of (1) the production of aluminium; (2) the properties of the metal, with which are included many test data relating to cold working and heat treatment; (3) light alloys for casting purposes; (4) light alloys of the duralumin type for working and heat treatment, including the results of tests; and (5) heavy aluminium alloys, *i. e.*, the so-called aluminium bronzes. In a number of appendices there are given analytical methods for aluminium, extracts from the French aeronautical specifications, and results of tests carried out by laboratories.

The density of aluminium is given as 2.60, despite the reliable work of Brislee in 1913 showing it to be 2.70±, depending on the treatment. The melting point is given as 650° C., instead of 658.7° C., and there are other similar errors, as well as contradictions of statements. There are many curves showing the results of tests, but it is impossible to ascertain from the text what possible accuracy these may have or what number of tests they are based on. The information given in regard to duralumin is of much value because of the present general interest in this type of alloy. Some of the micrographs are poor, and the methods of etching are lacking. It is difficult to outline well the contents of the book within the limits of this short review, but on the whole, despite its numerous deficiencies, the work is a valuable contribution to the literature of the aluminium industry. Books on aluminium and its light alloys are few, and while Colonel Grard's work may be welcomed as a book on aluminium as such, its chief value lies in the abundance of test results given.

Robert J. Anderson

Coal—Its Properties, Analysis, Classification, Geology, Extraction, Uses, and Distribution. By ELWOOD S. MOORE, M.A., PH.D. 462 pp. John Wiley and Sons., Inc., New York, 1922. Price, $5.00.

As stated by the author, this book was prepared in an attempt to satisfy the demand for a handy reference volume of coal. The book fills a distinct need, as the literature on coal is scattered and not very accessible to the average reader. The work covers a wide range of topics regarding coal, and the author is to be commended on the large amount of valuable information on coal that he has assembled and made available for ready reference. The numerous footnotes should be of value to the reader who desires to obtain more information on some of the topics than can be given in a one-volume work. The illustrations are unusually good.

The chapters on the origin of coal and the fossil flora of the coal-forming periods are exceptionally good. The chapter on chemical analysis of coal contains among other methods those of the American Society for Testing Materials, which are now almost universally used in this country by the better class of analytical laboratories. Three chapters, covering over 100 pages, deal with the coal fields of the world, and many maps showing the location of various coal fields are given. Other chapters of the book deal with physical and chemical properties of coal, varieties and ranks of coal, classification of coal, structural features of coal seams, prospecting for coal lands, mining, preparation, and uses of coal.

The worth of a book covering such a wide range of topics depends largely on the ability of the author to select information which is generally recognized as authoritative. In the preparation of the work the author has evidently searched the literature of coal very carefully, for the information presented is of high order and represents authoritative work on coal. So many valuable and interesting data on coal have been compiled and systematically arranged that no one interested in coal can afford to be without this volume.

W. A. SELVIG

Practical Chemistry of Coal and Its Products. By A. E. FINDLEY AND R. WIGGINTON. 144 pp. Benn Bros. Ltd., London, 1921. Price, 12s. 6d. net.

The title of this book would indicate the contents more clearly to the American mind if it were worded, "Analytical Methods for Coal and Its Products." The preface states that it embodies, with some additions, the laboratory course in fuel technology at Sheffield University. The various chapters deal with the analysis of coal and coke, with tar and tar products, ammonia liquor and other gas works products, and with gas analysis. Water analysis and pyrometry are also included. There are only 114 pages of actual text, so that the treatment of each subject is necessarily brief. The book gives methods in use in Great Britain which are not always the same as those used in the United States. Differences in analytical procedure are not important in some cases, since almost equally accurate results may be obtained by several methods. This is the case with the total sulfur in coal and the methods of water analysis, to cite two cases from this book. Many of the analyses used for coal products are proximate in their nature and the results vary with rather slight changes in technic. In this country committees of the American Chemical Society, the American Society for Testing Materials, and the American Gas Association have spent much effort in standardizing methods which should give comparable results in the hands of different operators. The methods given in this book are different from the standard American methods in many instances, and should not be used in this country if they are to be interpreted in terms of American practice. For instance, the methods for moisture and volatile matter in coal are about such as were used in America twenty years ago and lack the definiteness of the present standard methods. The book is a valuable one for those who wish the methods as used in Great Britain, but should be used with caution if results are to be compared with those obtained in ordinary American analytical practice.

ALFRED H. WHITE

Perfumes, Essential Oils, and Fruit Essences. By GEOFFREY MARTIN, D.Sc., F.I.C. viii + 138 pp. D. Van Nostrand Co., New York, 1921. Price, $3.50.

In the preface the author states that the purpose of this volume is to supply the requirement for a short and clear account of the principal scenting substances used in practice, especially in the soap industry, with practical directions for testing them so that the works chemist or manufacturer can speedily find the article he desires.

The work is evidently merely a compilation, in many cases of rather obsolete material. In the list of references cited on page 3, the second edition of "The Chemistry of Essential Oils," by E. J. Parry is given, whereas two editions have appeared since, and "Die Aetherische Oele," Gildemeister and Hoffman, is referred to as consisting of two volumes appearing in 1910, whereas the second volume appeared in 1913 and a third volume in 1916.

The book is divided into thirteen short chapters, the first of which embodies Erdmann's classification, which appeared in 1900. Since that time many new facts have been discovered.

The manufacture of essential oils is dismissed in two pages and is very superficial. Chapters 3, 4, and 5 deal with essential oils, animal perfumes and synthetics, respectively. A chapter on artificial fruit essences and esters occupies but three pages. The statistics on imports and exports, when given, are for 1910 and are consequently out of date.

A little more than one page each is devoted to tinctures and extracts and to the blending of perfumes, and four chapters deal with recipes for handkerchief and similar perfumes, and perfumes for soaps, for smelling salts and for sachet powders.

The analysis of essential oils is treated in a little over four pages, and is very inadequate.

Altogether the book is a disappointment, and it is difficult to see how it can be of great value to either the chemist or manufacturer who has access to the standard works on the subject.

E. K. NELSON

Technical Records of Explosives Supply, 1915-1918. VIII—Solvent Recovery. 19 × 28 cm. 22 pp. 8 illustrations. Ministry of Munitions and Department of Scientific and Industrial Research, London. H. M. Stationery Office, 1921. Price, 3s.

Solvents have come, in recent years, to be used in a great variety of industries, among them the explosives, pyroxylin plastics, photographic, pharmaceutical, varnish, oil, and rubber, not to mention the extraction of grease from garbage and suint from wool. Where the solvent occurs in the end operation in high concentrations the long known and well developed methods of distillation, with condensation, have afforded ready means of recovery, but where the manufacturing operations have been such that the solvent has become volatilized and diluted with large volumes of air few efforts have been made to recover it. As a consequence many hundreds of thousands of pounds of precious material, often representing the heaviest charge in the cost of production, are wasted annually, while at the same time fire and explosion risks, and unsanitary conditions are often created through the escape of these volatiles into the atmosphere at the factories.

This publication presents the data collected in the recovery of ether and alcohol vapors produced in the manufacture of cordite at the Gretna factory. This was accomplished by "housing in" the drying stoves and leading the vapor-laden air through liquid absorbents. Sulfuric acid, water, and cresol were each tested carefully as absorbents and the latter found so efficient when (under Bregeat, Brit. Patent 128,640) the details of plant operation had been developed that spent solvent was recovered at a rate equivalent in value to £282,000 annually by a recovery plant costing £80,000.

It is frankly stated that one of the objects of this report is "to encourage the adoption of solvent recovery among those who use volatile solvents even on a comparatively small scale, by an appeal to the same facts as decided its successful installation in propellant manufacture;" hence in addition to the 8 pages devoted to the data and technic at Gretna some 12 pages are given to theory, including "laboratory measurements" and "application of laboratory data," which supply a clear guide to manufacturers, and one that could be followed with profit by students in chemical engineering, while researches in which the methods are applied to other solvents and to other absorbents cannot but yield useful data and information.

CHARLES E. MUNROE

The Analysis of Fuel, Gas, Water, and Lubricants. By S. W. PARR, Professor of Applied Chemistry, University of Illinois. 3rd edition. $5^1/_2 \times 8$ in., xii + 250 pp., 54 illustrations, 14 tables of conversion factors. McGraw-Hill Book Co., Inc., New York, 1922. Price, $2.50.

This book is used as a text by students in chemistry, chemical engineering, and mechanical engineering in their junior year at the University of Illinois.

Coal classification, unit coal, coal sampling and analysis, calorimetric measurements, coal contracts, combustion of coal, storage, weathering, and spontaneous combustion cover 80 pages. Coke, wood, petroleum, alcohol, fuel gas, and flue gas are discussed in 32 pages. Boiler waters, their analysis, and treatment cover 42 pages. Lubricants and their analysis occupy 13 pages. Methods for coal analysis and for B. t. u. determination (44 pages), fuel gas analysis and calorimetric testing (16 pages), and flue gas analysis (3 pages) complete the treatise.

The book has value outside the field for which it was primarily written. Thoroughly up to date, it will find use in all testing laboratories, and will be used as a reference book by chemists and engineers who assist in the efficient use of fuel, water, and lubricants.

The probable error of the peroxide calorimeter should be mentioned. The constant temperature jacketed calorimeter used by the Bureau of Standards and by the Bureau of Mines is really more accurate than the adiabatic type in the hands of the average chemist, and should be mentioned. Instead of the method given in the chapter on ultimate analysis for calculating the hydrogen content of coal, the method in the Bureau of Mines *Technical Paper* **197**, "The Use of the Hydrogen-Volatile Matter Ratio in Obtaining the Net Heating Value of American Coals," is simpler and safer. The section on boiler waters is very good. The conversion factors are well chosen.

Attention is called to a few errors, some of which are important:

On p. 131, *M.* H. Wickhorst

On p. 132, lines 5 and 12, 0.833 instead of 1.20 (error in derivation).

The chemical costs in Table XX are not derived from the lime and soda prices stated on p. 132. Soda ash now costs $1.20 per 100 lbs.

On p. 219, Table XXII, line 8, 0.36 CaO should be 0.56.

JAS. O. HANDY

Zirconium and Its Compounds. By FRANCIS P. VENABLE. American Chemical Society Monograph Series. 173 pp. Chemical Catalog Co., Inc., New York, 1922. Price, $2.50.

A study of this monograph brings to the mind, perhaps, two main thoughts with regard to zirconium. First, the large amount of research which awaits the investigator, work which is by no means so easy and simple as the uninitiated might be inclined to think. Second, the large number of very varied uses to which the element and its compounds have been recommended, by various workers, as revealed by studying the list of patents.

The general material of the book is of a very concentrated nature, which shows that the literature has been carefully searched and abstracted. In several cases, it would seem that the cutting down has been carried much too far. Under the heading of zircon, the description and concentration of zircon sand might have been given in more detail. The chapter upon analytical methods could have been extended very much more. Very complete statements of the methods employed for the determination of this element would have been of great use to those who have little knowledge along this line and who are unable to refer to original papers.

The complex nature of zirconium compounds is well shown under a discussion of the sulfates. Zirconium sulfite, also, would seem to be a very interesting substance since the normal salt, and normal salts of this metal are not common, is stated to be formed by the action of such a weak acid as sulfurous acid upon zirconium hydroxide which is a very weak base. In addition to this there are a large number of similar interesting facts. It is to be hoped that this publication will give the average chemist more insight to the chemistry and the possible uses of this comparatively common element, which, unfortunately, is looked upon by so many as being too rare for much industrial work.

C. JAMES

Soap-Making Manual. A Practical Handbook on the Raw Materials, Their Manipulation, Analysis and Control in the Modern Soap Plant. By E. G. THOMSSEN, PH. D. 243 pp. D. Van Nostrand Co., New York, 1922. Price, $4.00.

As the subtitle indicates, this book deals with many of the materials, methods, and machines involved in the manufacture of soap.

The chapter on raw materials treats this phase of the subject from the standpoint of the factory man and makes no attempt to go thoroughly into the properties of these substances after the manner of the well-known handbooks of oils, fats, and waxes.

The descriptions of soap-making processes are better than many that have found their way into print and they represent some of the practices that are followed by soap makers.

A considerable number of soap formulas are given, some of which are of more or less doubtful value, not that soap could not be made in accordance therewith but because they do not represent the best practice. The author makes the statement that comparatively little hardened oil has been used in America in soap making. The amount that has been so used is larger than he appears to have knowledge of.

The chapters on glycerol recovery and analytical methods will give a good idea of some of the methods that are in use.

The book contains a few mistakes, most of which will be at once apparent to a chemist. One that might lead to a little confusion is the figure giving the Na_2O equivalent of 1 cc. normal acid solution as 0.02905 gram.

Several tables of useful information are given. Those for glycerol do not agree among themselves, nor does either of them agree with the commonly accepted values.

The book will be of interest to soap makers.

MARTIN HILL ITTNER

COMMERCE REPORTS

Notice—*Commerce Reports are received by all large libraries and may be consulted there, or single numbers can be secured by application to the Bureau of Foreign and Domestic Commerce, Department of Commerce, Washington, D. C. The regular subscription rate for these Commerce Reports mailed weekly is $3.00 per year (10 cents per single copy), payable in advance to the Superintendent of Documents, Government Printing Office, Washington, D. C.*

May

An interesting report of the French **bauxite** industry in 1921 has been made by Consul Wesley Frost and copies may be had by application to the Iron and Steel Division of the Bureau of Foreign and Domestic Commerce. (P. 284)

Official Spanish import statistics show that the United States continues to be the chief source of supply for **petroleum** and petroleum products imported into Spain. (P. 297)

By decree of March 17, 1922, the government monopoly on the importation of **copper vitriol** into Switzerland has been removed, effective July 15, 1922. (P. 310)

There is said to be a good market for **caustic soda** in Chile, both in wholesale quantities and in smaller packages. (P. 320)

The development of the Esthonian **oil-shale** industry is described and the total output of Esthonian oil shale for 1919 is given as 9484 long tons, 45,417 long tons in 1920, and 93,157 long tons in 1921. The government is very optimistic as to the important future for oil from Esthonian shale and is anxious to interest foreign capitalists therein. (Pp. 357–8)

The French export restriction on crude **methanol,** rectified methanol and **acetone** has been removed, and these products may be exported and reëxported without special authorization. (P. 378)

By a decree of March 30, 1922, the temporary surtax on **gasoline** and other petroleum products imported into France has been reduced to 10 francs per hectoliter. (P. 379)

An order of the Controller of Customs of New Zealand increases the duty on certain **petroleum** products. (P. 379)

Poland's **alcohol** production for the past year is said to amount to 40,000,000 liters, of which 15,000,000 will be available for export. (P. 383)

Mining operations are being carried on by the Soviet Mining Council in developing the **radium** resources of the Ferghana Valley and transporting the radioactive ore to the extracting works recently erected for this purpose at the Bondujee Chemical Works. (P. 384)

Tests recently completed by the Sociedad Nacional de Agricultura of Rio de Janeiro, Brazil, show that an **alcohol** mixture can be used successfully as a motor fuel and at lower cost than gasoline. (Pp. 402–3)

Samples of **acid-proof cloth** suitable for laboratory aprons, coats, leggings, gloves, etc., recently perfected in Lancashire have been received by the Textile Division of the Bureau of Foreign and Domestic Commerce. Further particulars may be obtained by addressing that Division. (P. 410)

There are five mills in Italy manufacturing **artificial silk,** all of which use the viscose process. (P. 415)

By Australian Customs Proclamations the **exportation** of metals, alloys, and minerals is prohibited. (P. 443)

As a quarantine measure against agricultural pests, the Peruvian government has prohibited the importation of **cottonseed** into that country. (P. 443)

A bill has been introduced in the Congress of Uruguay which proposes a government monopoly on the production, importation, or sale of **alcohol.** (P. 443)

The National University of La Plata, Argentine, plans to construct and instal a **hydraulic laboratory** on the water front of La Plata. (P. 448)

Because of the importance of the Cuban import trade in **caustic soda, bleaching powder,** and **hydrochloric acid,** the uses to which these chemicals are put in Cuba are described. (Pp. 448–9)

All the nitrate firms in Chile are producers or possible producers of **iodine** but the Combinacion de Yodo restricts the free production of this drug. With a view to increasing the use of iodine the combination has offered prizes for the discovery of new uses for it. (P. 449)

It is reported that **poppy-seed oil** is used for illumination and fuel in Smyrna. (P. 450)

An exhaustive report entitled "**Mineral Deposits** and Industries in South Africa" is on file in the Bureau of Foreign and Domestic Commerce and may be obtained for consultation by addressing the Western European Division. (P. 456)

The **lignite** and **peat** deposits in Italy are described. (P. 487)

Rules for **oil** exploitation on federal lands in Mexico are cited. (P. 493)

A new schedule of import duties on **petroleum** and **paraffin** is announced in Cyprus. (P. 506)

The new tariff of the Virgin Islands of the British West Indies places a duty on **oils** and **turpentine.** (P. 507)

A licensing system for the importation of **dyestuffs** into Japan has been proposed, but if adopted it will not be effective until three months after passage and advance notice of at least 30 to 60 days will be given the public. (P. 507)

A number of important changes, for the most part reductions, have been made in the minimum duties of the new Spanish customs tariff, affecting principally **mineral oils** and industrial **starches.** (Pp. 508–9)

Changes in the Spanish export duties have also been made with respect to **copper ores,** cassiterite, copper precipitate, and metallic **bismuth.** (P. 509)

The German government control of **light oil, crude benzene, benzene, toluene,** and related products was removed, effective April 1, 1922. (P. 510)

The action of the Brazilian government in making various loans and concessions to encourage the manufacture of **caustic soda** in Brazil will undoubtedly work to the detriment of American exportation of caustic soda to Brazil. (P. 513)

The Latin American Division of the Bureau of Foreign and Domestic Commerce has available the following reports on the **mineral deposits** and industries of Brazil which will be sent to the Bureau's district or coöperative offices upon request for the numbers given: 54,555, monazite sand; 54,559, manganese; 54,507, mica; 54,508, iron; 54,509, oil; 54,557, translation of the Brazilian mining law; 55963, mineral industries of Sao Paulo. (P. 513)

The **tin** mining industry of the Dutch East Indies is described. (P. 551–2)

The **petroleum** trade of Palestine is reviewed. (Pp. 556–7)

It is believed that the establishment of agencies in Aden would give American concerns an excellent opportunity to secure the small but steady market for **paints** in this district. (P. 582)

Foreign experts are being added to the staff connected with the Industrial Experiment Stations of Japan to find a solution for the shortage of **raw materials,** the chief weakness of Japan's industrial and commercial life, and an appropriation has been made for the Oska Industrial Experiment Station to ascertain to what extent artificial products can be used as substitutes for natural resources. (P. 588)

SPECIAL SUPPLEMENTS ISSUED

DUTCH GUIANA
GUATEMALA
Trade of ADEN, Fiscal Year 1920–21
Trade of CZECHOSLOVAKIA in 1920
Trade of DENMARK in 1920
Trade of HONGKONG in 1920
Trade of WESTERN SAMOA in 1920

STATISTICS OF EXPORTS TO THE UNITED STATES

BAGDAD—(P. 317)
  Gum, tragacanth and arabic

GREECE—(P. 385)
  Opium
  Olive oil

RED SEA DISTRICT—(P. 386)
  Gum myrrh

SYRIA—(P. 386)
  Olive oil
  Licorice root

CANADA—(P. 491)
  Pulp wood
  Wood pulp

TAMPICO, MEXICO—(P. 557
  Petroleum

ADEN, ARABIA—(P. 582
  Gums
  Wax

CURRENT PUBLICATIONS

NEW BOOKS

Analysis of Fuel, Gas, Water, and Lubricants. S. W. Parr. International Chemical Series. 3rd edition. 250 pp. Price, $2.50. McGraw Hill Book Co., Inc., New York.

Analysis of Nonferrous Alloys. F. Ibbotson and L. Aitchison. 2nd edition. 242 pp. Price, 12s. 6d. Longmans, Green & Co., London.

Atomic Structure: The Structure of the Atom: Notes on Some Recent Theories. Stephen Miall. Price, 1s. 6d. Benn Bros., Ltd., London.

Butter: Principles and Practice of Butter-Making. G. L. McKay and C. Larsen. 3rd edition, largely rewritten. 405 pp. 133 figures. Price, $3.00. John Wiley & Sons, Inc., New York.

Ceramics: Manuel de Céramique Industrielle. D. Arnaud and G. Franche. 2nd edition, revised and rewritten. 614 pp. 306 figures. Price, 39 fr. Dunod, Paris.

Chemical Examination of Water, Sewage, Foods, and Other Substances. J. E. Purvis and T. R. Hodgson. 2nd edition. 346 pp. Price, 20s. net. Cambridge University Press, London.

Chemistry: An Advanced Course of Instruction in Chemical Principles. Arthur A. Noyes and Miles S. Sherrill. 310 pp. Illustrated. Price, $4.00. The Macmillan Co., New York.

Chemistry: Second Year College Chemistry. William H. Chapin. 311 pp. 44 figures. Price, $1.50. John Wiley & Sons, Inc., New York.

Colloids: Laboratory Manual of Colloid Chemistry. Harry N. Holmes. 127 pp. 31 figures. Price, $2.00. John Wiley & Sons, Inc., New York.

Gas: Elektrische Behandlung von Gasen. Henri Silbermann. 348 pp. Price, $3.20. Max Jänecke, Leipzig.

Heat Engines: Modern Practice in Heat Engines. Telford Petrie. 264 pp. Illustrated. Price, $5.00 net. Longmans, Green & Co., New York.

Iron: On the Electro-Deposition of Iron. W. E. Hughes. Bulletin No. 6, Department of Scientific and Industrial Research. 50 pp. Price, 6s. 6d. H. M. Stationery Office, London.

Inorganic Type Formulas and Their Relationships. Herbert O. Smith, Compiler. 6 pp. Price, 15 cents. D. Van Nostrand Co., New York.

Leather: The Principles of Leather Manufacture. H. R. Procter. 2nd edition. 696 pp. Illustrated. Price, $10.00. D. Van Nostrand Co., New York.

Metallography. C. H. Desch. 3rd edition. 440 pp. Price, 16s. Longmans, Green & Co., London.

Nitrate Facts and Figures, 1922. A. F. Brodie James. 15 pp. Price, 6s. net. F. C. Mathieson & Sons, London.

Nutrition: The Newer Knowledge of Nutrition; the Use of Food for the Preservation of Vitality and Health. Emer Verner McCollum. 2nd edition, entirely rewritten. 449 pp. Illustrated. Price, $3.80. The Macmillan Co., New York.

Organic Chemistry: A Textbook of Organic Chemistry. A. Bernthsen. New edition, revised to date by J. J. Sudborough. 924 pp. Price, $3.75. D. Van Nostrand Co., New York.

Organic Chemistry: Travaux Pratiques de Chimie Organique. Fritz Ulmann. Translated by Raymond Cornubert. 2nd French edition. 262 pp. Illustrated. Price, 18 fr. Dunod, Paris.

Outline of Science: A Plain Story Simply Told. John Arthur Thomson, Editor. 296 pp. Illustrated. Price, $3.75. G. P. Putnam's Sons, New York.

Paper Mill Chemist. Henry P. Stevens. 2nd edition, revised and enlarged. 325 pp. 67 illustrations. Price, $4.00. D. Van Nostrand Co., New York.

Petroleum Industry: A Brief Survey of the Technology of Petroleum. Edited by A. E. Dunstan. 346 pp. Price, 14s. 6d. net. The Institution of Petroleum Technologists, London.

Pharmaceutical Chemistry: Lehrbuch der Pharmazeutischen Chemie. Schmidt. 6th edition. 2nd volume, part 1. Price, 154 mk. Dunod, Paris.

Physical Chemistry: Some Physico-Chemical Themes. A. W. Stewart. 418 pp. Price, 21s. Longmans, Green & Co., London.

Physics: Dictionary of Applied Physics. Sir Richard Glazebrook, Editor. Five volumes. Vol. 1. Mechanics Engineering Heat. 1067 pp. Price, $15.00. The Macmillan Co., New York.

Proteins and the Theory of Colloidal Behavior. Jacques Loeb. International Chemical Series. 292 pp. Illustrated. Price, $3.00. McGraw-Hill Book Co., Inc., New York.

Soil: The Nature and Properties of Soils: A College Text of Edaphology. T. Lyttleton Lyon and Harry O. Buckman. Agricultural Science Series. 588 pp. Illustrated. Price, $3.25. The Macmillan Co., New York.

Steel: The Electrometallurgy of Steel. C. C. Gow. 367 pp. Illustrated. Price, $7.50. D. Van Nostrand Co., New York.

Sulfur and Sulfur Derivatives. Harold A. Auden. 101 pp. Illustrated. Price, $1.00. Isaac Pitman & Sons, New York.

Town Gas Manufacture. R. Staley. 108 pp. Price, 2s. 6d. net. Sir Isaac Pitman & Sons, Ltd., London.

Welding: Modern Methods of Welding, as Applied to Workshop Practice, Describing Various Methods. J. H. Davies. 281 pp. Illustrated. Price, $6.00. D. Van Nostrand Co., New York.

Women in Chemistry. **Bureau of Vocational Information.** 272 pp. Price, paper, $1.10; cloth, $1.60. Bureau of Vocational Information, New York.

World Metric Standardization. Aubrey Drury and Others. 524 pp. Price, $5.00. World Metric Standardization Council, 681 Market St., San Francisco, Cal.

NEW JOURNAL

Journal of Scientific Instruments. Acting Editor, E. H. Rayner. Published monthly by the Institute of Physics with the coöperation of the National Physical Laboratory. Price, 2s. 6d. per issue. The Institute of Physics, 10 Essex St., London, W. C. 2, England.

RECENT JOURNAL ARTICLES

Accelerators. Lothar E. Weber. *India-Rubber Journal*, Vol. 63 (1922), No. 20, pp. 17–21.

Ammonia: Catalyse et Synthèse de l'Ammoniaque. Paul Firmin. *L'Industrie Chimique*, Vol. 9 (1922), No. 99, pp. 147–51.

Blast Furnace: Control of Silicon in the Blast Furnace. S. L. Goodale. *Blast Furnace and Steel Plant*, Vol. 10 (1922), No. 5, pp. 274–78.

Cellulose: Some Observations on the Behavior of Oxidized Cellulose. Edmund Knecht and F. P. Thompson. *Journal of the Society of Dyers and Colourists*, Vol. 38 (1922), No. 5, pp. 132–36.

Colloids: Les Colloides et leurs Principales Applications. Paul Razous. *L'Industrie Chimique*, Vol. 9 (1922), No. 100, pp. 200–02.

Color in Relation to Dyeing. J. Merritt Matthews. *Color Trade Journal*, Vol. 10 (1922), No. 6, pp. 229–35.

Dyes: The After-Chroming of Wool. Alan A. Claflin. *American Dyestuff Reporter*, Vol. 10 (1922), No. 12, pp. 397–400.

Dyes: The Relation between Chemical Constitution and Antiseptic Action in the Coal-Tar Dyestuffs. Thomas H. Fairbrother and Arnold Renshaw. *Journal of the Society of Chemical Industry*, Vol. 41 (1922), No. 9, pp. 134*t*–44*t*.

Formaldehyde Tannage. Arthur M. Hey. *Journal of the Society of Leather Trades' Chemists*, Vol. 6 (1922), No. 4, pp. 131–36.

Fuel: Using Fuel in Open-Hearth Furnaces. Herbert F. Miller, Jr. *The Iron Age*, Vol. 109 (1922), No. 22, pp. 1495, 1555–56.

Leather: The Factors Influencing the Plumping of Hides in Tan Liquors. W. R. Atkin. *Journal of the Society of Leather Trades' Chemists*, Vol. 6 (1922), No. 4, pp. 138–44.

Porcelain: Economic Handling of Materials in Porcelain Manufacture. A. P. Ball. *Journal of the American Ceramic Society*, Vol. 5 (1922), No. 5, pp. 235–47.

Porcelain: Beryl as a Constituent in High Tension Insulator Porcelain. Robert Twells, Jr. *Journal of the American Ceramic Society*, Vol. 5 (1922), No. 5, pp. 228–34.

Steel: Effect of Quality of Steel on Case-Carburizing Results. H. W. McQuaid and E. W. Ehn. *Forging and Heat Treating*, Vol. 8 (1922), No. 5, pp. 243–47.

Steel: Reduction of Fuel Wastes in the Steel Industry. F. G. Cutler. *Blast Furnace and Steel Plant*, Vol. 10 (1922), No. 5, pp. 291–94.

Zinc: A Study of the Throwing Power and Current Efficiency of Zinc Plating Solution. W. Grenville Horsch and Tyler Fuwa. *Brass World*, Vol. 18 (1922), No. 5, pp. 146–52.

GOVERNMENT PUBLICATIONS

Notice—*Publications for which price is indicated can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C. Other publications can usually be supplied from the Bureau or Department from which they originate.*

Bureau of Foreign and Domestic Commerce

Asbestos: World Production and Trade. Prepared in Western European Division by C. C. Miller. *Trade Information Bulletin* **20.** 10 pp. Issued April 20, 1922.

Markets for Chemicals in the Netherlands East Indies and British Malaya. J. A. Fowler. *Trade Information Bulletin* **31.** 18 pp. Issued June 12, 1922.

The German and Alsatian Potash Industry. Prepared in the Western European Division. *Trade Information Bulletin* **18.** 11 pp. Issued April 19, 1922.

Bureau of Mines

Mercury Poisoning. R. R. Sayers. *Reports of Investigation* **2354.** 6 pp. Issued May 1922.

Methods for Testing Petroleum Products Adopted by the Interdepartmental Petroleum Specifications Committee. A Handbook for Inspecting Laboratories. *Technical Paper* **298.** 58 pp. Paper, 10 cents.

Mica. Oliver Bowles. *Reports of Investigations* **2357.** 46 pp. Issued May 1922.

Recent Articles on Petroleum and Allied Substances. Compiled by E. H. Burroughs. *Reports of Investigations* **2348.** 21 pp. Issued April 1922.

Recovery of Gasoline from Uncondensed Still Vapors. D. B. Dow. *Reports of Investigations* **2344.** 26 pp. Issued April 1922.

Separation of Palladium and Platinum by Means of Dimethylglyoxime. O. W. Davis. *Reports of Investigations* **2351.** 2 pp. Issued May 1922.

Smokeless Fuel for Salt Lake City. G. St. J. Perrott and H. W. Clark. *Reports of Investigations* **2341.** 18 pp. Issued April 1922.

The Analytical Distillation of Petroleum and Its Products. E. W. Dean, H. H. Hill, N. A. C. Smith and W. A. Jacobs. *Bulletin* **207.** 82 pp. Paper, 15 cents.

The Sulfur Dioxide Leaching Process. Method for Treating Nonsulfide Copper Ores as Developed at the Southwest Experiment Station of the Bureau of Mines. C. E. van Barneveld and E. S. Leaver. *Reports of Investigations* **2350.** 15 pp. Issued May 1922.

The Tannic Acid Method for the Quantitative Determination of Carbon Monoxide in the Blood. R. R. Sayers and W. P. Yant. *Reports of Investigations* **2356.** 7 pp. Issued May 1922.

Congress

Helium Gas. A bill authorizing the conservation, production, and exploitation of helium gas, a mineral resource pertaining to the national defense, and to the development of commercial aeronautics, and for other purposes. **H. R. 11549.** 5 pp. Introduced by Mr. Kahn, May 4, 1922, and referred to the Committee on the Public Lands.

Muscle Shoals. A bill to provide for the manufacture of explosives for the use of the Army and Navy, to provide for the manufacture of fertilizer for agricultural purposes, to incorporate the Federal Chemical Corporation, and for other purposes. S. 3585. 22 pp. Introduced by Mr. Norris, May 11, 1922, and referred to the Committee on Agriculture and Forestry.

Naval Petroleum Reserve No. 3, Wyoming. Letter from the Secretary of the Interior and the Secretary of the Navy in response to a Senate Resolution of April 15, 1922, transmitting information relative to negotiations with private parties for the operation of lands in Naval Petroleum Reserve No. 3, Wyoming. Senate Document 191. 3 pp. April 20, 1922.

Offer for Properties at Muscle Shoals, Ala. Letter from the Secretary of War transmitting offer received from Charles L. Parsons, of Washington, D. C., covering certain properties at Muscle Shoals, Ala. House Document 220. 4 pp. April 4, 1922.

Tariff Act of 1922, bill (H. R. 7456) to provide revenue, to regulate commerce with foreign countries, to encourage industries of the United States, and for other purposes, as reported to the Senate April 11, 1922. 179 pp. Senate Document 187.

Tariff Bill, report to accompany S. Con. Res. 21 (for printing of H. R. 7456, to provide revenue, to regulate commerce with foreign countries, to encourage industries of the United States, and for other purposes, as Senate Document); submitted by Mr. Kiess. H. Rp. 911. 1 p. April 19, 1922. (Corrected print.)

Congressional Committees

Muscle Shoals Propositions. Amendments to Engstrum Offer. Hearings before the Committee on Military Affairs, House of Representatives, 67th Congress, 2nd session. 6 pp.

Report from the Committee on Military Affairs, to accompany H. R. 11903. Report No. 1084. 57 pp. June 9, 1922.

Patents. Hearings before the Committee on Patents, United States Senate, on S. 3325 and S. 3410 bills to amend Sections 4886 and 4887 of the Revised Statutes relating to Patents. April 6, May 1, 3, and 4, 1922. 302 pp.

Bureau of Standards

Carbon Monoxide in Products of Combustion from Natural Gas Burners. J. V. Brumbaugh and G. W. Jones. *Technologic Paper* 212. Paper, 10 cents.

Metallographic Etching Reagents: II—For Copper Alloys, Nickel, and the Alpha Alloys of Nickel. H. S. Rawdon and M. G. Lorentz. *Scientific Paper* 435. Paper, 15 cents.

Recommended Specifications for Quicklime and Hydrated Lime for Use in Cooking of Rags for Manufacture of Paper. *Circular* **96** (Reprint). 5 pp. Paper, 5 cents.

The Redwood Viscometer. W. H. Herschel. *Technologic Paper* **210.** Paper, 10 cents.

The Solubility of Dextrose in Water. R. F. Jackson and C. G. Silsbee. *Scientific Paper* **437.** Paper, 5 cents.

Bureau of the Census

Animal and Vegetable Fats and Oils: Production, Consumption, Imports, Exports, and Stocks by Quarters, Calendar Years 1919, 1920, and 1921. Prepared under supervision of W. L. Austin, assisted by H. J. Zimmerman. 16 pp. 1922.

Department of Agriculture

Some Changes in the Composition of California Avocados during Growth. C. G. Church and E. M. Chace. *Department Bulletin* **1073.** 22 pp. Paper, 5 cents. Issued May 12, 1922.

Geological Survey

Chromite in 1921. Edward Sampson. Separate from Mineral Resources of the United States, 1921, Part I. 3 pp. Published May 15, 1922.

Copper in 1920. General Report. H. A. C. Jenison. Separate from Mineral Resources of the United States, 1920, Part I. 53 pp. Published May 16, 1922.

Fuel Briquets in 1921. W. F. McKenney. Separate from Mineral Resources of the United States, 1921, Part II. 5 pp. Published May 26, 1922.

Gold, Silver, Copper, Lead, and Zinc in the Eastern States in 1921. Mines Report. J. P. Dunlop. Separate from Mineral Resources of the United States, 1921, Part I. 7 pp. Published May 12, 1922.

Graphite in 1921. L. M. Beach. Separate from Mineral Resources of the United States, 1921, Part II. 6 pp. Published June 5, 1922.

Peat in 1921. K. W. Cottrell. Separate from Mineral Resources of the United States, 1921, Part II. 2 pp. Published June 6, 1922.

Surface Water Supply of the United States 1918. Part VII—Lower Mississippi River Basin. N. C. Grover, Robert Follansbee and R. C. Rice. Prepared in coöperation with the States of Colorado and Kansas. *Water Supply Paper* **477.** 38 pp. Paper, 5 cents.

Navy Department

Medical Aspects of Gas Warfare. G. H. Mankin. United States Naval Medical Bulletin Published for the Information of the Medical Department of the Service. **16** (April 1922), 641–9.

Public Health Service

Carbon Tetrachloride. A Drug Proposed for the Removal of Hookworms, with Special Reference to Its Toxicity for Monkeys when Given by Stomach Tube in Repeated Doses. G. C. Lake. *Public Health Reports* **37** (May 12, 1922), 1123–6.

Physiological Effects of Exposure to Low Concentrations of Carbon Monoxide. R. R. Sayers, F. V. Meriwether and W. P. Yant. *Public Health Reports* **37** (May 12, 1922), 1127–42.

Tariff Commission

Preliminary Summary of Census of Dyes and Coal-Tar Chemicals, 1921. *Tariff Information Series* **25.** 73 pp. 1922.

Tariff Information Surveys. Second revised edition, 1922. On articles in Paragraphs 51 to 63, inclusive, of the Tariff Act of 1913 and related articles in other paragraphs. **Pigments, Paints and Varnishes.** 206 pp. Paper, 15 cents.

War Department

Report on the Fixation and Utilization of Nitrogen. Prepared by the Nitrate Division, Ordnance Office, War Department, assisted by the Fixed Nitrogen Research Laboratory, Department of Agriculture. No **2041.** 353 pp. 1922.

MARKET REPORT—JUNE, 1922

[SUPPLIED BY DRUG & CHEMICAL MARKETS]

Demand for chemical products of all kinds is in a very unstable condition and is subject to wide variations at the slightest hint at a change in basic conditions. The promise of a gradual increase seen in business in the month of May has failed utterly to materialize during June. Apparently there has been no definite change in conditions to bring this about, and the only excuse that is offered by the trade is the threadbare one of "summer dullness." The continued uncertainty of the tariff situation has had much to do with failure of business to increase as was expected and there is much dissatisfaction in the chemical trade as in all other lines of business with the obstructionist tactics adopted by the Senate in handling the measure. The general belief is that a definite, even unfavorable, tariff would be preferable to the continued bickering over rates that is now going on.

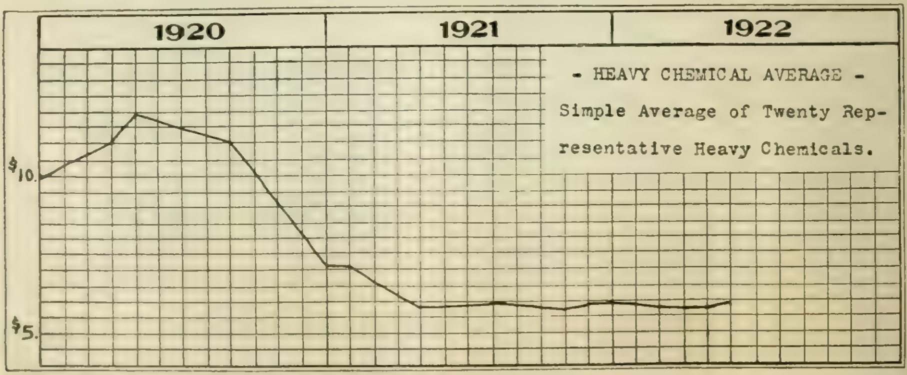
Speculative interest in the market has died away to a noticeable extent and those items which attracted this interest last month are consequently weak. Imported barium salts and yellow prussiate of soda are outstanding examples of this. Barium chloride gradually eased off during the early part of the month following the announcement that another domestic producer would be able to offer within the month considerable reductions under prices then quoted. Barium carbonate failed to advance as speculators believed it would, and has shown a further weakening with that of the chloride. Yellow prussiate of soda has weakened from the peak in spite of the extremely strong statistical position it occupies and sales have been made at 21 cents in spite of the fact that most holders are refusing bids at less than 23 cents. Estimates from various sources are well agreed that stocks in New York do not exceed twenty-five tons and nothing can be had from England for some months. Yellow prussiate of potash is similarly situated.

Manufacturers' price changes have been unimportant with few exceptions. Potassium nitrate was reduced 1 cent per pound on competition with importers and a smaller comparative reduction was made on iron-free aluminium sulfate by one manufacturer in competition with German goods, although others have failed to follow. American muriate of potash has sold in competition with German in New York. Makers advanced sodium acetate, and copper sulfate has been advanced sharply on active export demand resulting from a contract made by consumers in southern Europe with a group of producers here. Lead acetate was reduced by makers. Bleaching powder is firmer.

Imported products have been generally inactive with prices tending downward. Ammonium chloride, potash alum, sodium nitrate, and iron-free sulfate of aluminium are lower from importers. Potassium permanganate is firmer. Camphor is firmer in spite of the heavy supplies in a few hands here. Potassium carbonate is advancing on more active demand. Beeswax, both crude and refined, is sharply higher and very scarce in the New York market. Wood alcohol is slightly firmer. Formaldehyde and glycerol are weak.

The market for coal-tar products shows little activity. The refiners of tar advanced their prices on benzene and solvent naphtha early in the month on the continued scarcity of supplies. At the same time the announcement was made that drums will be quoted in the future at 5 cents per gallon above the tank car prices for any quantity. Naphthalene is weaker in outside hands although refiners quote 7 cents firm for flake in large quantity. Price cutting to force sales in the face of sharp competition between makers has greatly interfered with improvement in business in intermediates. Aniline oil, beta-naphthol, dimethylaniline, H acid, and R salt have been particularly subject to this condition and makers are exerting every effort to force onto the market more of these materials than it can possibly absorb. The entrance of new manufacturers of these items into the field when the market was at its low point has tended to render the condition caused by over-production of these items much worse. The market for para-nitroaniline has been more or less disturbed by the prospect of a new manufacturer in this field, but so far nothing further than rumors have come into the market. Dyes are generally inactive.

Oils have shown little activity during the month and prices seem to have ceased their recent steady advance. Linseed oil is declining on lower seed prices. Cod and menhaden oils from the new catch are coming into the market in small lots and speculative trading in futures is fairly active. Cottonseed oil is extremely dull with supplies small in all directions and with little interest from consumers. Trading in next winter's oil is proceeding slowly at prices below the present market for nearby oil. Turpentine is advancing at present and seems firm at the successive levels. Rosin went sharply higher late in May but arrivals shortly after the first of June forced sellers to reduce prices below the levels quoted before the advance.



Courtesy of Drug & Chemical Markets

FIRST-HAND PRICES FOR GOODS IN ORIGINAL PACKAGES PREVAILING IN THE NEW YORK MARKET

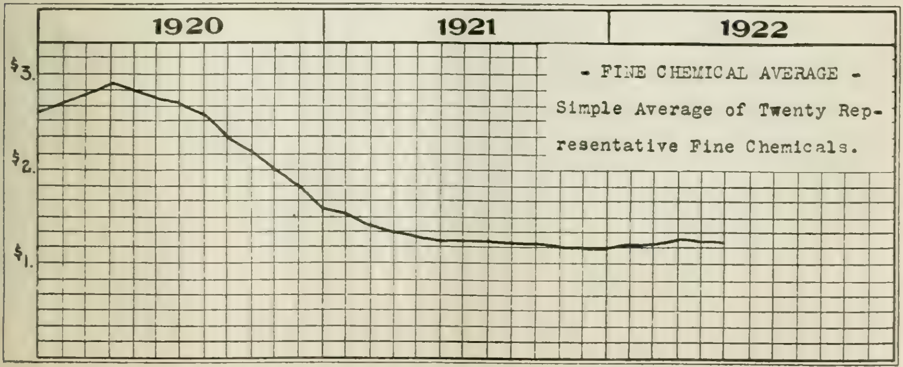
INORGANIC CHEMICALS

	June 1	June 15	Jan. 1922
Acid, Boric, cryst. bbls...... lb	.11¾	.11¾	.12¾
Hydrochloric, comm'l. 20° lb.	.01¼	.01¼	.01¼
Hydrofluoric, 30% bbls..lb.	.07	.07	.07
Hydriodic, sp. gr. 1.150...lb.	2.25	2.25	2.00
Nitric, 42°, cbys. c/l wks.lb.	.06	.06	.06
Phosphoric, 50% tech.....lb.	.08	.08	.10
Sulfuric, C. P............lb.	.07	.07	.07
66° tks. wks........ton	16.00	16.00	16.00
Oleum 20%.........ton	19.00	19.00	19.00
Alum, Ammonia, lump........lb.	.03½	.03½	.03½
Potash, lump............lb.	*.03	*.03	*.03½
Chrome............lb.	.06½	.06½	.07
Soda, ground............lb.	.03½	.03½	.03½
Aluminium Sulfate (iron-free).lb.	.02½	.02½	.02½
Ammonium Carbonate, pwd...lb.	.07	.07	.08
Chloride, white gran......lb.	.07¾	.07¾	.07½
Ammonia, anhydrous ....lb.	.30	.30	.30
Ammonia Water, drums, 26°...lb.	.07½	.07½	.07½
Arsenic, white...............lb.	.07¼	.07¼	.06½
Barium Chloride............ton	*100.00	*95.00	*53.00
Nitrate.................lb.	*.06	*.06	*.07
Barytes, white..............ton	33.50	33.50	28.00
Bleaching Powd., 35%, works ....100 lbs.	1.60	1.60	2.25
Borax, cryst., bbls............lb.	.05½	.05½	.05¾
Bromine, pure, wks...........lb.	.23	.23	.23
Calcium Chloride, fused, f.o.b. N. Y...................ton	24.50	24.50	28.75
Chlorine, liquid..............lb.	.06	.06	.06
Copper Sulfate..........100 lbs.	6.00	6.00	5.55
Iodine, resublimed...........lb.	4.20	4.20	3.80
Lead Acetate, white crystals...lb.	.10½	.10½	.11
Nitrate.................lb.	.15	.15	.15
Red....................lb.	.08	.08	.08
White (Carb.)............lb.	.07¼	.07¼	.07¼
Lime Acetate...........100 lbs.	1.75	1.75	1.75
Magnesium Carbonate, tech...lb.	.06	.06	.06
Magnesite, calcined..........ton	55.00	55.00	55.00
Phosphorus, yellow...........lb.	.25	.25	*.27
Red....................lb.	*.26	*.26	*.30
Plaster of Paris.............bbl.	4.25	4.25	4.25
Potassium Bichromate........lb.	.10	.09¾	.10½
Bromide, imported.......lb.	*.16	*.16	*.13
Carbonate, calc., 80–85%.lb.	*.04¾	*.04¾	*.04½
Chlorate, cryst...........lb.	*.06½	*.06½	*.05½
Hydroxide, 88–92%......lb.	*.05¾	*.05¾	*.06
Iodide, bulk............lb.	3.30	3.30	2.90
Nitrate.................lb.	.08	.07	.08
Permanganate, U. S. P....lb.	*.15	*.15	*.15
Prussiate, red...........lb.	*.85	*.85	*.29
Yellow..............lb.	*.32	*.33	*.24½
Salt Cake, bulk.............ton	21.00	21.00	17.00
Silver Nitrate...............oz.	.48	.48	.44½
Soda Ash, 58%, bags.....100 lbs.	*1.80	*1.80	*1.85
Caustic, 76%, N. Y..100 lbs.	3.80	3.75	3.80
Sodium Acetate..............lb.	.05	.05	.04
Bicarbonate.........100 lbs.	2.00	2.00	2.00
Bichromate.............lb.	.07¼	.07¼	.07¾
Bisulfite, powd...........lb.	.04¼	.04¼	.04¼
Chlorate................lb.	.06¾	.06¾	.07½
Cyanide, 96–98%........lb.	.25	.25	.28
Fluoride, tech............lb.	.10	.10	.09½
Hyposulfite, bbls.....100 lbs.	3.25	3.25	3.50
Nitrate, 95%........100 lbs.	2.80	2.70	2.32½
Nitrite..................lb.	.09½	.09½	.06½
Prussiate, yellow.........lb.	.23	.22	.16½
Phosphate (di-sod.),tech..lb.	.04	.04	.04¼
Silicate, 40°.............lb.	.01	.01	.01¼
Sulfide, 60%, fused.......lb.	.04	.04	.05
Strontium Nitrate............lb.	*.08	*.08	*.10
Sulfur, flowers...........100 lbs.	3.00	3.00	2.75
Crude, mines.......long ton	14.00	14.00	16.00
Tin Bichloride, 50% sol'n......lb.	.10½	.10½	.09¾
Oxide...................lb.	.38	.38	.37
Zinc Chloride, U. S. P.........lb.	.35	.35	.35
Oxide, bbls..............lb.	.08	.08	.08

ORGANIC CHEMICALS

	June 1	June 15	Jan. 1922
Acetanilide, U. S. P. bbls.......lb.	*.30	*.30	*.29
Acid, Acetic, 28 p. c.......100 lbs.	2.37½	2.37½	2.37½
Glacial..............lb.	.08	.08	.10
Benzoic, U. S. P........lb.	.55	.55	.60
Carbolic, cryst., U. S. P., drs...............lb.	.14	.14	.12
50- to 110-lb. tins....lb.	.19	.21	.18
Citric, crystals, kegs......lb.	*.44½	*.44½	*.43
Oxalic, cryst., bbls., wks...lb.	.14	.14	.14
Pyrogallic, resublimed....lb.	1.60	1.60	1.75
Salicylic, U. S. P.........lb.	.26	.26	.24
Tannic, U. S. P., bbls....lb.	.65	.65	.75
Tartaric, cryst., U. S. P...lb.	*.28½	*.28½	*.25
Acetone, drums..............lb.	.08	.10	.12
Alcohol, denatured, complete.gal.	.27	.27	.45
Ethyl, 190 proof, bbls....gal.	4.65	4.65	4.75
Amyl Acetate...............gal.	1.90	1.90	2.00
Camphor, Jap, refined, cases...lb.	.75	.78	.90
Carbon Bisulfide, c/l..........lb.	.06	.06	.06½
Tetrachloride............lb.	.10	.10	.10½
Chloroform, U. S. P., drums...lb.	.30	.30	.43
Creosote, U. S. P.............lb.	.40	.40	.40
Cresol, U. S. P...............lb.	.14	.14	.14
Dextrin, corn............100 lbs.	2.99	2.99	2.70
Imported Potato.........lb.	.09	.09	.06½
Ether, U. S. P., 100 lbs.........lb.	.14	.14	.14
Formaldehyde, bbls...........lb.	.08	.08	.10½
Glycerol, dynamite, drums....lb.	.12½	.12½	.14½
Methanol, pure, bbls.........gal.	.72	.72	.75
Methylene Blue, med.........lb.	3.00	3.00	4.00
Petrolatum, light amber......lb.	.04½	.04½	.05¼
Pyridine....................gal.	1.75	1.75	1.75
Starch, corn, pow'd......100 lbs.	2.47	2.47	2.13
Potato, Jap..............lb.	.07	.07	.06½
Sago.....................lb.	.03½	.03½	04.

*Resale or Imported (not an American makers' price).



Courtesy of Drug & Chemical Markets

OILS, WAXES, ETC.

	June 1	June 15	Jan. 1922
Beeswax, pure, white.........lb.	.33	.40	.33
Castor Oil, No. 3.............lb.	.11	.11	.10½
Ceresin, yellow..............lb.	.07½	.07½	.07½
Corn Oil, crude. tanks, mills...lb.	.09½	.09½	.06¾
Cottonseed Oil, crude, f. o. b. mill ....lb.	.10	.10	.07
Linseed Oil, raw, c/l ....gal.	.84	.82	.69
Menhaden Oil, crude, mills...gal.	.38	.38	.35
Neat's-foot Oil, 20°..........lb.	.22	.22	.16¾
Paraffin, 128–130 m. p., ref.....lb.	.03¾	.03¾	.05
Rosin, "F" grade, 280 lbs....bbl.	6.20	5.65	5.30
Rosin Oil, first run..........gal.	.36	.36	.36
Shellac, T. N................lb.	.78	.82	.66
Sperm Oil, bleached winter, 38°.....................gal.	1.69	1.59	1.70
Stearic Acid, double pressed...lb.	.09½	.09½	.09¾
Tallow Oil, acidless...........lb.	.10	.10	.10
Turpentine, spirits of........gal.	.96	.99	.82½

METALS

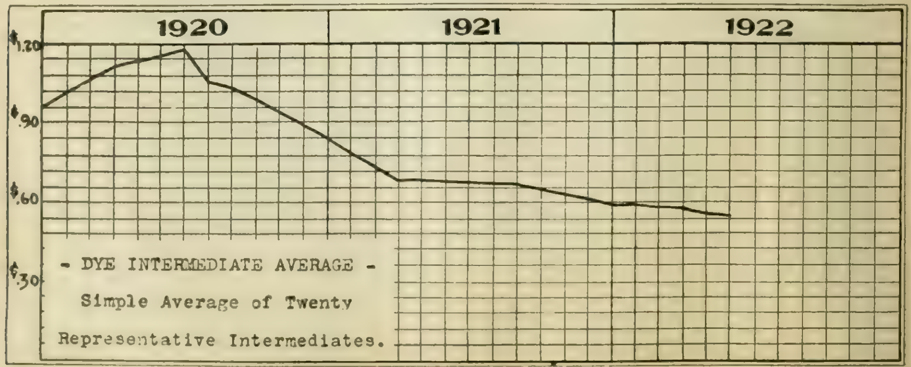
	June 1	June 15	Jan. 1922
Aluminium, No. 1, ingots.....lb.	.17½	.17½	.17
Antimony, ordinary......100 lbs.	5.37½	5.30	4.55
Bismuth....................lb.	2.10	2.10	1.80
Copper, electrolytic..........lb.	.14	.13⅞	.13⅞
Lake...................lb.	.14	.13⅞	.13¾
Lead, N. Y..............100 lbs.	5.60	5.75	4.70
Nickel, electrolytic...........lb.	.39	.39	.45
Platinum refined, soft........oz.	85.00	87.00	78.00
Quicksilver, flask......75 lbs. ea.	55.00	55.00	52.00
Silver, foreign...............oz.	.71⅜	.71⅜	.65¼
Tin.........................lb.	.32⅛	.31½	.32¾
Tungsten Wolframite....per unit	2.00	2.00	2.00
Zinc, N. Y..............100 lbs.	5.50	5.75	5.20

FERTILIZER MATERIALS

	June 1	June 15	Jan. 1922
Ammonium Sulfate, expt..100 lbs.	3.50	3.50	2.60
Blood, dried, f. o. b. N. Y....unit	3.65	3.65	3.50
Bone, 3 and 50, ground, raw..ton	28.00	28.00	30.00
Calcium Cyanamide, unit of ammonia	2.25	2.25	2.25
Fish Scrap, dried, wks......unit	3.50 & .10	3.50 & .10	3.25 & .10
Phosphate Rock, f. o. b. mine:			
Florida Pebble, 68%.....ton	3.00	3.00	5.00
Tennessee, 78–80%......ton	6.00	6.00	8.00
Potassium Muriate, 80%....unit	*.60	*.60	*.75
Tankage, high-grade, f. o. b. Chicago...............unit	3.65 & .10	3.65 & .10	3.00 & .10

COAL-TAR CHEMICALS

	June 1	June 15	Jan. 1922
Crudes			
Anthracene, 80–85%.........lb.	.75	.75	.75
Benzene, pure, tanks ....gal.	.29	.30	.29
Naphthalene, flake...........lb.	.06½	.06	.07½
Phenol, drums...............lb.	.14	.14	.11
Crudes (*concluded*)			
Toluene, pure, tanks.........gal.	.30	.30	.30
Xylene, 2 deg. dist. range, tanks..................gal.	.45	.45	.45
Intermediates			
Acids:			
Anthranilic..............lb.	1.10	1.10	1.10
Benzoic, tech............lb.	.50	.50	.50
Cleve's.................lb.	1.50	1.50	1.50
Gamma..................lb.	1.80	1.80	2.25
H.......................lb.	.80	.75	1.00
Metanilic...............lb.	1.00	1.00	1.60
Monosulfonic F..........lb.	2.30	2.30	2.30
Naphthionic, crude.......lb.	.60	.60	.65
Nevile & Winther's.......lb.	1.25	1.25	1.30
Picric..................lb.	.20	.20	.25
Sulfanilic...............lb.	.22	.22	.26
Tobias'.................lb.	1.50	1.50	2.00
Aminoazobenzene............lb.	1.15	1.15	1.15
Aniline Oil.................lb.	.14	.14	.17
Aniline Salt................lb.	.20	.20	.25
Anthraquinone (sublimed)....lb.	1.35	1.35	1.50
Benzaldehyde, tech...........lb.	.65	.65	.45
U. S. P.................lb.	1.40	1.40	1.25
Benzidine Base..............lb.	.85	.85	.90
Benzidine Sulfate............lb.	.70	.70	.70
Diaminophenol...............lb.	5.50	5.50	5.50
Dianisidine.................lb.	4.50	4.50	4.75
p-Dichlorobenzene...........lb.	.17	.17	.15
Diethylaniline...............lb.	.60	.60	.90
Dimethylaniline..............lb.	.34	.34	.40
Dinitrobenzene..............lb.	.20	.20	.21
Dinitrotoluene...............lb.	.20	.20	.25
Diphenylamine..............lb.	.58	.58	.58
G Salt.....................lb.	.65	.65	.70
Hydroquinol................lb.	.90	.90	1.35
Monochlorobenzene..........lb.	.10	.10	.10
Monoethylaniline............lb.	1.00	1.00	1.00
b-Naphthol, dist.............lb.	.23	.23	.30
a-Naphthylamine............lb.	.30	.30	.30
b-Naphthylamine............lb.	.95	.95	1.05
m-Nitroaniline..............lb.	.72	.72	.85
p-Nitroaniline..............lb.	.75	.75	.77
Nitrobenzene (Oil Mirbane)...lb.	.10	.10	.10
p-Nitrophenol...............lb.	.75	.75	.75
o-Nitrotoluene..............lb.	.12	.12	.15
p-Nitrotoluene..............lb.	.60	.60	.70
m-Phenylenediamine.........lb.	1.00	1.00	1.10
p-Phenylenediamine..........lb.	1.50	1.50	1.60
Phthalic Anhydride..........lb.	.35	.35	.38
R Salt.....................lb.	.55	.50	.60
Resorcinol, tech.............lb.	1.30	1.30	1.50
U. S. P.................lb.	1.75	1.75	2.00
Schaeffer's Salt. ....lb.	.60	.60	.70
Sodium Naphthionate........lb.	.60	.60	.70
Thiocarbanilide..............lb.	.35	.35	.40
Tolidine (base)..............lb.	1.15	1.15	1.20
Toluidine, mixed............lb.	.30	.30	.30
o-Toluidine..................lb.	.16	.16	.20
p-Toluidine..................lb.	1.00	1.00	1.10
m-Toluylenediamine..........lb.	.95	.95	1.10
Xylidine....................lb.	.42	.42	.40



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EDITORIALS

The War in Washington

IF YOU are among those who believe the war is really over, you need to be awakened. It is true that war is over in the sense that our soldiers no longer fight, but while men still die from the effects of the war the enemy continues his fight in Washington.

The fight in the main is carried on in secret in the ways so well developed in the days prior to the Great War, but now and again the enemy shows himself and can be seen like a snake making his way through the grass. What makes us most indignant is the ease with which this fight is carried to places high in our Government. We all knew there would be a "war after the war," but no one would have believed that our own government departments would be among the first to weaken the line of defense. Would any true American have predicted that chemists and the chemical industry would be subjected to unfair discrimination?

Antagonism to Chemical Warfare Service

The many chemists who were urged to enter the service and upon whom the military establishment depended for its most effective means of offense and defense were mustered out with greater rapidity than any other branch of the service. Not until a fight was made were the officials brought to realize the folly of scattering the information gained at such great cost and the grave danger involved in dispensing entirely with the services of chemists. Even to-day the Chemical Warfare Service is far from secure. Officials have refused to be convinced of the proved humanitarian aspects, the simplicity and economy of chemical warfare. Army officers of the old school have endeavored to turn their backs on the utility of nontoxic smokes, lachrymators, incendiaries, and other chemical weapons not to be classed with poison gases. Notwithstanding the demoralizing effect of uncertain War Department policy and limited funds, the Chemical Warfare Service has continued its program of research.

Suppression of Technical Report

When the Technical Committee was appointed to serve the Limitation of Armament Conference, it was thought that chemical warfare was in such hands that at least a fair hearing would be secured. So far there is no evidence that the report of this committee of experts was ever given consideration. The State Department announced that all reports would be printed before the treaties were offered to Congress, but this technical report has been suppressed, and, like the others, never printed. It is significant that efforts to secure the release of this report for publication have been unsuccessful.

Attack on Textile Alliance

[illegible] the [illegible] of the Textile Alliance. In spite of its satisfactory record of service to American users of reparation dyes, the State Department [illegible] relations with the Textile Alliance. The State Department has steadfastly [illegible] that if American users wish reparation dyes they should [illegible] importers. Whose interest does the State Department propose to protect?

Renewal of Patent Convention

Soon came a request from the State Department to the President that the Treaty Convention of 1909 be renewed. This was protested by chemists but without avail, for that Convention has now been renewed and provides that if German citizens are not required to operate under their American patents, Americans owning German patents will not be required to operate in Germany. Several powerful corporations not chemical in nature find this to their advantage, but it may some day be distinctly to the disadvantage of our great chemical industry.

Plans to Destroy Foundation

Now comes the letter of the President directing the Alien Property Custodian to recover from the Chemical Foundation the German patents purchased from the Custodian during the war. It is inconceivable that the President could have appreciated the full significance of this step, or certainly he would not have taken it. Did he consult the chemists, the chemical manufacturers, the medical profession, or only those who are either misinformed or under foreign influence?

The Chemical Foundation has become the nucleus of our organic chemical industry. Because of licenses granted by the Foundation $100,000,000 has been invested. Upon the assurance of scores of attorneys, chemical manufacturers have laid out programs of development, many of which have been followed notwithstanding industrial depression. At the time the Foundation was incorporated it received general commendation. No licensee has objected to the treatment received from the Foundation. Because nonexclusive licenses are granted, monopolies have been broken and the ultimate consumer has benefited thereby. Recently the president of the Foundation appeared before the subcommittee of the Judiciary Committee of the Senate and offered himself for cross-examination. It is notable that no one accepted the challenge.

Our highest legal authorities have said *"that Congress is not empowered by the Constitution to pass laws for the protection of authors and inventors, except as a means of promoting the progress of science and the useful arts,"* and this is so expressed in the Constitution. American chemical patents, particularly product patents, owned by foreigners have been used quite generally not "to promote science and the useful arts" in our country, but for the sole purpose of preventing such development by manufacture here, leaving to them a protected field for their exploitation. Many contend that this abuse of our patent law should deprive owners of their patent rights.

However, the legal phases will be decided in court. Of course the Chemical Foundation has refused to obey the demand of the Alien Property Custodian and in due time civil suits will be instituted. The sale of these patents was made in accordance with the Trading-with-the-Enemy Act as amended and upon executive order of the President who had been given the power by Congress to make such disposition of enemy property as seemed to be in the best interests of the country.

Value of Patents

The value of these patents? Certain members of Congress who have mentioned ten, twenty, or thirty millions state that this would be their value if these patents were used to create monopolies. Since these patents were used by their original owners for that purpose, they may place such valuation upon them. As administered by the Chemical Foundation they can have but a very small fraction of that value. These patents are not resold by the Foundation, but nonexclusive licenses are granted, sometimes without royalty or upon royalties rarely exceeding 5 per cent of the market value of goods manufactured. The Foundation has granted to the Government free licenses on all patents held by it. The benefits derived from competition are illustrated by the case of salvarsan. Prices under the German monopoly were $4.50 per dose to the physician, $2.50 per dose in quantity to the Government. There are now several licensees in this country manufacturing a satisfactory product and as a consequence the price has fallen to $1.50 and about 30 cents, respectively.

While the Chemical Foundation is a privately managed enterprise, it is as nearly an altruistic institution as one will ever find engaged in business. The president receives no salary. Of the $500,000 capital stock, $400,000 is preferred nonvoting; $100,000 is common, carries the voting power and is not owned in excess of two shares by any individual or corporation. There is a voting trust and the trustees are men of such high character that it seems unnecessary to dwell on the point, even where political issues are involved. Any money earned in excess of 6 per cent is devoted to research, education, and eventually to the development of worthy American inventions.

The Motive?

With this background, we ask—as does the public in the case of crime—what can be the motive? What is actuating our officials, allied with a party whose cornerstone is protection, to take so many unusual steps against the chemical industry? Some argue that it is the smaller politicians who desire to discredit officials of the former administration. Surely an industry and all that goes with it for public benefit and welfare would not be sacrificed for so small a price. We do not believe that personalities are involved. Others say that the Department of Justice must make a showing in the prosecution of so-called "war frauds" and give the public something to think about other than the much-discussed record of the Attorney General in the Morse case. But here again one can hardly think that all that comes from the encouragement of chemistry in this country would be sacrificed in such a manner. Again, others say, "Oh, well, it will be a good thing to return these patents to government control, for they will not be given back to Germany but administered in future for the benefit of our industry and research." This is fraught with unusual dangers. There has already been introduced a bill authorizing the return of property held by the Alien Property Custodian valued at $10,000 or less, and Section 12 of the Trading-with-the-Enemy Act provides that with Congress rests the responsibility of disposing of property held by the Alien Property Custodian. No dependence can be placed on what Congress will do with this property. We have as yet no reason to believe that Congress appreciates its value to America, and by value we mean things that cannot be appraised in dollars. If these patents are returned to the Alien Property Custodian we must look forward to being ourselves returned to the power of the monopolies we learned to know and despise during the war.

German Visits

The Department of Justice admits that it has been visited by representatives of German interests, although claiming that this visit had nothing to do with recovery of patents—that the Germans sought advice relative to instituting suits growing out of the seizure. The Department stated that the demand for the patents is the most economical method of fighting a number of suits filed against the United States Treasurer by the Chemical Foundation. Even in these days of economy one cannot believe this explanation. The suits in question are friendly suits to establish the ownership and the amounts of money deposited with the United States Treasurer by manufacturers licensed by the Federal Trade Commission before the patents became the property of the Chemical Foundation. These are not federal funds, but money paid for license fees to be transmitted to the owner, and there is an accounting to be made both for the time prior to and since the sale of the patents to the Foundation.

What, then, is back of all this uproar? Without doubt there is a strong political aspect in the action against the Foundation. If the sale had been made with Republicans in power, the present administration no doubt would have resorted to friendly conference. As it is, there will be a deal of unfortunate publicity which will tend to hurt the chemical industry regardless of its relations with the Foundation. At the moment, not only the Foundation, but chemistry stands convicted in the eyes of the public without a hearing. But the most sinister influence originates in Germany and is ably forwarded by adherents in this country. Most of the editorial comment favorable to the action taken by the President is to be found in foreign language newspapers and subsidized sheets known to be either under the domination of German influence or already identified with interests unfriendly to the American chemical industry. Hyphenated societies, with objects and principles of old unchanged, have passed approving resolutions.

Who Has the Backdoor Key?

The man who managed the presidential campaign of our present Secretary of State is now an attorney for the American representative of the German Cartel. In the Department of Justice is ex-Senator Thomas who consistently fought any attempt to encourage the chemical industry in this country while he held office. One alert, resourceful and crafty importer has unobstructed access to the floor of the House by virtue of being one of its ex-members. He has not hesitated to abuse this privilege in furthering his own interests. He goes at will to give his misinformation to those who will listen, while the representatives of American industry must stop at the door. Representatives of the Interessengemeinschaft, "I. G.," are said to have had their desks in the offices of United States senators. A favorite source of information for the opposition and those who have been misled by it is a man who admitted before a congressional committee that he represented German interests in this country for years prior to the war, was especially active under the direction of Boy-Ed, and received a large salary for which he did many despicable things.

Why is it that Americans have such difficulty in being heard by some high government officials? Why is it that some of our government departments seem willing to sacrifice American industry, chemical and otherwise, if by any stretch of imagination its progress might be detrimental to foreign interests? Why is it that the President has not directed the Alien Property Custodian also to recover other property sold by his predecessor, even though sold to the Government? This includes more than 6000 patents sold to the Army and Navy for $100,000 in order that munitions of war could be produced without infringement, and the wireless patents, including the Sayville tower, sold to the Navy for $140,000. The Government will have to settle for their use if these sales are rescinded, as they must be if the Government is consistent and the chemical patents are returned.

Dye Embargo

The letter of the President was nicely timed to have an influence upon the dye embargo. Republican senators were placed in an embarrassing position, and if it did not influence their vote, certainly it made it difficult for them to fight for the measure as they would have liked to do. As for the Democrats, they voted strictly on party lines, without regard to the merits of the measure and apparently oblivious of their previous position when the embargo was urged by President Wilson. The embargo will be offered for another vote when amendments to the bill are considered before its final passage. Its temporary defeat constitutes another chapter in this history of antagonism toward the American industry.

Temperamentally we are not inclined to become excited, but here is a situation that thoroughly arouses Americans. The story has been retailed to us by friend and foe. We remain fully confident of the ultimate outcome. Surely justice, proverbially blind, can detect and thwart this latest menace. Meanwhile the opposition continues with misstatements, insinuations, and clever intrigue. What are *you* going to do about it?

Speak Up

The chemical profession must speak up. We are now on the defensive, and must fight for our rights or be reconciled to lose them forever. Chemistry is not seeking favors for faithful service in times of peace and war. It asks no largess for all that it has done in strengthening our industrial position and for its many contributions to the art of healing. No pay is asked for the part played in making life safer, longer, easier, and more enjoyable.

But chemistry and the chemical industry have earned a right to live and develop. They demand that they be not made the football of politicians. So long as the life and future of chemical research, the industry and the part it plays in national defense are menaced, we must continue our campaign of education. We must return to the defense and strengthen our lines, although fighting may not be a pleasant occupation. Many of us would rather remain unmolested in our laboratories, turn our energies to constructive work, plan and encourage fundamental research, stimulate development, and in general pursue the many paths along which our profession leads us.

The present fight promises to be a fight to the finish. The Department of Justice is committed on the front page of the country's papers. It will not turn back nor will we. Our fight cannot be left to a few. It will require all the numbers we can command. Can we count on you?

The Journal of Physical Chemistry

THE FUTURE of the *Journal of Physical Chemistry*, which has made an enviable reputation for itself, has long concerned many members of the Society. Financial support having been recently offered, the question of a plan for future development has engaged the attention of a committee of the Division of Physical and Inorganic Chemistry. The report made to the Division at Birmingham was sent out to the members of the Council for a letter ballot. As a result steps are now being taken to learn to what extent and in what way the Chemical Society of London may join with the American Chemical Society in the future management and publication of the *Journal of Physical Chemistry*. The report stated that the direction of the *Journal of Physical Chemistry*, if undertaken, was to be without expense to either society. The hope was expressed that it might be internationalized and made the outstanding English language journal in this field.

The question will undoubtedly come again before the Council at Pittsburgh, and it is hoped that members will come well versed in the situation and prepared to vote in accordance with the wishes of those whom they represent.

Some believe that physical chemistry does not require the stimulation of emphasis which usually follows the establishment of a special journal. Others argue that any support which might be obtained for the *Journal of Physical Chemistry* on the new plan could better be given the *Journal of the American Chemical Society* in order to strengthen its position as the general research journal of the Society, rather than restrict its field. Still others feel that if another journal is to be taken under the auspices of the Society for the purpose of relieving the pressure upon our present journals, it should be a special one dealing with organic, analytical, inorganic or biological chemistry. There is a further argument that if the journal of the Society could be enlarged the special papers which would otherwise go to the *Journal of Physical Chemistry* would be very sure to receive a much larger circulation, would therefore come to the attention of a greater variety of chemists, and presumably stimulate an interest in physical chemistry among a great many who could not see the new publication.

We have as our first desire the progress of chemistry in America and we may be called upon to take important action at Pittsburgh with respect to the publication of general research in future. The Councilors owe it to themselves and to their Sections to become thoroughly informed!

Plan to Go to Pittsburgh

THE PITTSBURGH Meeting (September 4 to 9, 1922) promises to be one of the most important in our history. The present situation in America demands careful consideration. We can reach well-considered conclusions only if we have a large number of chemists in attendance, and if Councilors take the trouble to learn the pleasure of their Sections before they come to vote on actions and policies of the Society.

The Pittsburgh Section has put a great deal of thought and effort into the arrangements, the scientific programs will be of unusual interest, and as usual there will be a valuable opportunity to meet and discuss with your fellows the problems of greatest interest to you. There should be no less than two thousand in attendance. Plan to be one of the number!

IN THE biography of Andrew Carnegie we find that it was his appreciation of chemistry which enabled him to obtain an early lead over his competitors and which practically formed the basis of his great success. In this instance it was research upon raw materials which counted. The chemist found that a better product could be obtained from cheaper raw materials than the mill was in the habit of employing. Every manufacturer knows what it means to produce better goods from cheaper materials, and where great tonnage is involved the return upon the investment in scientific work runs into unusually satisfactory figures.

The U. S. Government Explosives Plant C, Nitro, West Virginia[1]

III—The Manufacture of Nitric Acid

By March F. Chase[2]

L. L. Summers & Co., 140 Nassau St., New York, N. Y.

THERE are two general processes for the manufacture of nitric acid; the usual method consisting of the decomposition of sodium nitrate by sulfuric acid, and the newer method by the fixation of atmospheric nitrogen. The latter method is not in general use and is applicable only under special conditions. The plants are costly and take considerable time to build. At the time of building the Nitro Plant the Government was already contemplating the erection of two or three large nitrogen fixation plants. Two of these plants were finally built, one at Sheffield, Alabama, and the other at Muscle Shoals. Two others were started but the work on them had not progressed very far at the time of the Armistice and the projects were immediately abandoned. The sodium nitrate method was selected for Nitro.

Sodium Nitrate Method

This method of nitric acid manufacture consists in brief of the following steps:

1—The decomposition of sodium nitrate by the action of sulfuric acid, the action being promoted by external heat.

2—The cooling and condensing of the nitric acid gases generated in the first step.

3—The absorption of the noncondensable gases in water or sulfuric acid.

Nitric acid yields from good plant operation may be safely calculated at 92 per cent of the theoretical; that is, approximately 65.5 lbs. of 100 per cent HNO_3 per 100 lbs. of 96 per cent nitrate of soda.

The nitrate of soda should be of the standard commercial quality, containing 96 per cent or more $NaNO_3$. If strong nitric acid is wanted, apparatus should be provided for drying the nitrate, as otherwise a stronger decomposing acid is needed.

The sulfuric acid used in decomposing the nitrate is usually of 66° Bé. grade. If the nitrate is not dried 95 per cent acid may be used. Usually the ratio of nitrate to 66° Bé. acid will be from 1 : 1.05 to 1 : 1.1.

The best fuel will depend upon the relative availability of gas, oil or coal. All are equally efficient as regards actual manufacture, but the first two, of course, are of advantage so far as labor is concerned.

In a properly equipped modern plant, the labor item need not be a large factor of cost, for a few men can easily handle a number of retorts.

The only by-product from nitric acid manufacture is niter cake. Under certain conditions this product has a value. This value lies in the fact that, in order to have the residue in stills in liquid form so that it may be easily run out, an excess of sulfuric acid over the theoretical quantity is used. The cake therefore contains enough acid sodium sulfate to give a total cake acidity corresponding to about 30 per cent of free sulfuric acid.

This cake may be used in certain instances, such as steel pickling, in place of sulfuric acid.

The most common use, however, and the one usually to be recommended under the proper conditions, is in the manufacture of muriatic acid and salt cake. Of course, for the economic success of this use it is necessary that there be a market for muriatic acid and salt cake (or Glauber salt). In such case, however, a good profit can be shown.

In case there is no use contemplated for the niter cake,

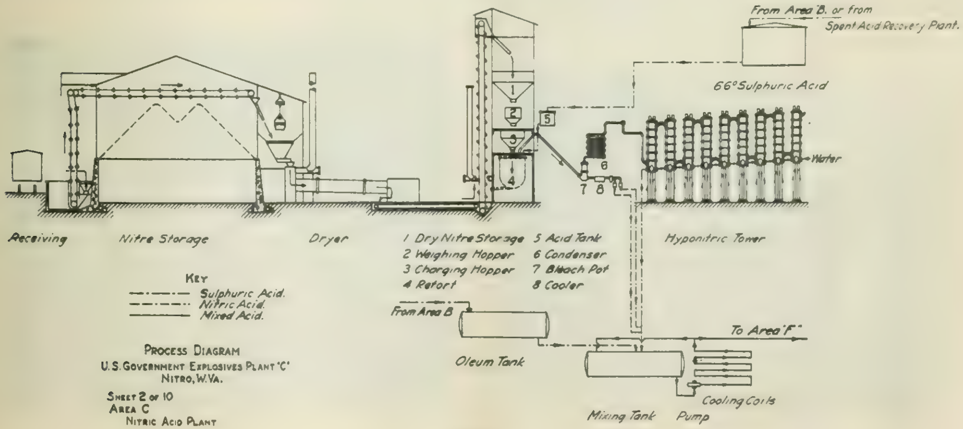

Fig. 1

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[1] Received June 22, 1922.

[2] Consulting Engineer; formerly Assistant Director of U. S. Government Explosives Plants; formerly member of War Industries Board.

[illegible] locating the plant that proper sewerage facilities exist for the discharge of the cake.

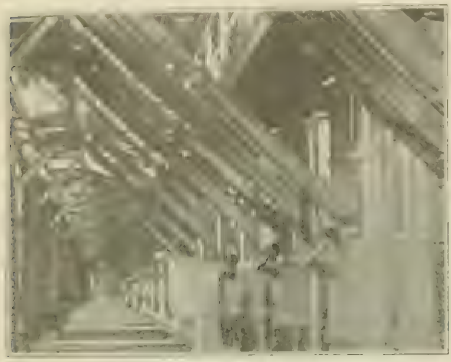

Fig. 2—[illegible] Interior of Retort House

Decomposition of Sodium Nitrate

The decomposition is carried out in a cast-iron retort or still. Long experience has shown the most efficient form of a still to consist of a vertical pot with a hemispherical bottom, provided with a bottom outlet for the "tapping out" of the still residue (niter cake). These stills are made in two sections, the lower constituting the body of the retort and the upper the top or lid. This upper portion is made slightly conical in shape and contains the proper openings for the introduction of nitrate and sulfuric acid, and for the outlet of the gases generated.

The retort is set in fire brick with a fire box for heating with gas, oil or coal.

Cooling and Condensing of Nitric Acid

This is accomplished in water-cooled, acid-resisting pipes. There are several forms of such condensers on the market, but engineering opinion favors the type known as the standard acid-resisting or government type condenser. This [illegible] of a number of return bends, made of a highly resistant alloy, and cooled externally by water sprays. This particular type is less subject to trouble than the submerged type of condenser, and is also generally believed to be more efficient because use is made of the evaporation of [illegible]

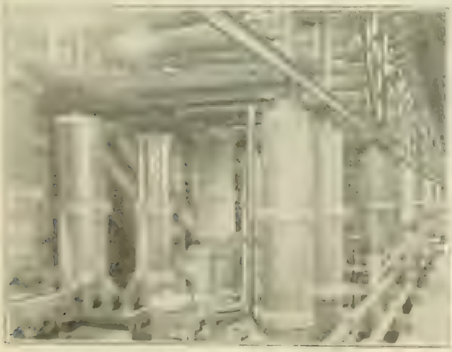

Fig. 4—[illegible]

Attached to and made a part of the condenser is usually a so-called bleach pot. This is a small acid-resisting iron pot,

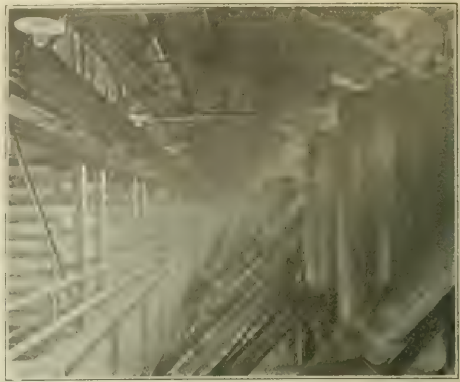

Fig. 3—Condenser Pipes and Acid Charging Tanks

packed with chemical rings. It is so set that the hot nitric acid gases from the retort pass into and through it, entering at the bottom and leaving at the top, before they enter the condenser proper. Also all acid formed in the condenser flows into the pot, entering at the top and leaving at the bottom. The effect of this countercurrent flow of gas and acid is (1) to cool slightly the gas entering the condenser, and (2) to remove the greater part of the lower oxides of nitrogen contained in the condenser acid, giving a practically pure, nearly water-white, product.

From the bleach pot the acid passes into the cooling pipes and thence to the product lines. In the best plants these product lines are two in number, one for the strong nitric acid which is formed during the greater part of the run, and one for the weaker acid formed near the end of a charge.

Absorption of Uncondensable Gases

The uncondensable gases, which consist principally of nitrogen peroxide, are absorbed in modern plants in chemical stoneware towers, called hyponitric towers. Experience has shown that there should be a ratio of standard

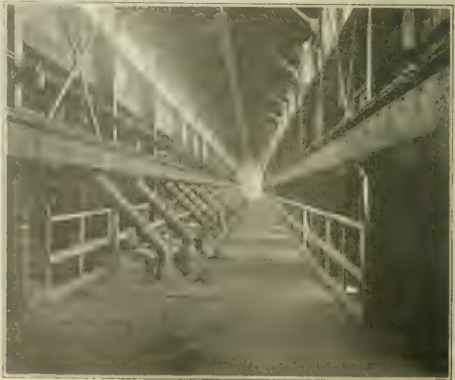

Fig. 5—Tops of Retorts

towers to standard retorts of 9 : 12, in order to get the maximum recovery of nitric acid.

Towers are usually constructed of chemical stoneware and the standard size is about 15 ft. in height by 2 ft. 6 in. in diameter. Absorption may be in water or, if a weak mixed acid can be utilized, in sulfuric acid. In either event, the absorbing medium is started over the final tower and is then handled by pulsometers over each of the towers in turn, countercurrent to the flow of the gas.

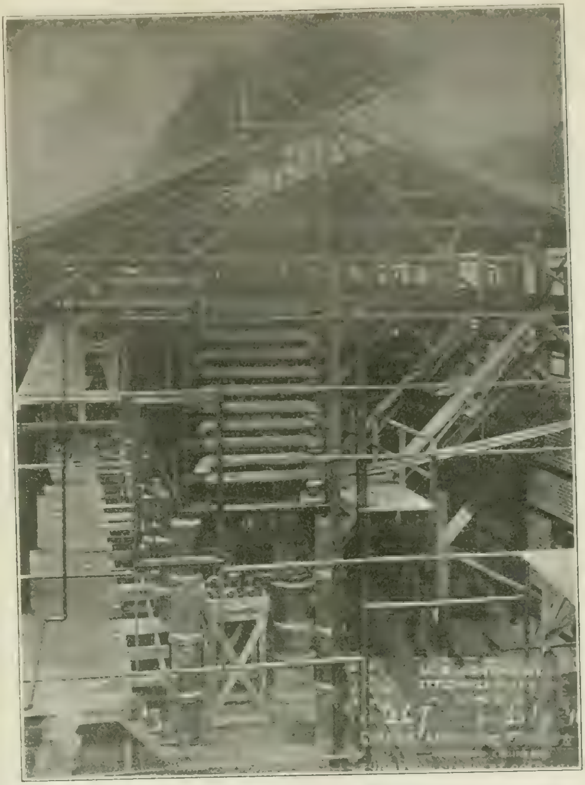
Fig. 6—End of Retort Building, Showing Bleach Pots and Condenser Coolers

The Nitro Plant

The nitric acid plant at Nitro was designed and operated with the view of utilizing the entire production in the form of mixed acid. On account of the large quantity of spent acid that would be recovered from the subsequent process of nitration, it was highly desirable that the product from the nitric acid plant contain as little water as possible. The stronger the nitric acid produced the less concentration was necessary for the spent acid. Considerable data had previously been collected in regard to the strength of nitric acid that could be produced in plants of design similar to that which it was contemplated to use at Nitro. The results of these determinations are given in the form of a curve, Fig. 7. The nitric acid plant was divided into four units of identical construction. Certain of the buildings, such as the niter storehouse and dryer buildings, served two units. Each unit contained twenty-four retorts, making a total of ninety-six. Of these units No. 1 was started April 15, 1918, and finished September 18, 1918; No. 3 was started March 15, 1918, and finished November 8, 1918; No. 2 was started June 1, and No. 4 on July 3. Work was stopped on these two units on November 15, No. 3 being 97.5 per cent complete and No. 4, 71 per cent complete.

The process employed was the nitrate process outlined above. While the apparatus was new only in a few particular features, it was designed, perhaps to a greater degree than in any other nitric plant then in existence, to make use of the information which had been obtained in the last few years on the intensive manufacture of nitric acid. This care in design was taken with a particular view to labor saving in operation and to ease of maintenance.

Beginning with the arrival of bagged nitrate, the procedure was as follows:

Bags of nitrate were unloaded to a platform at the height of a car floor, dumped, and elevated by bucket elevator which delivered to storage. The empty bags were trucked to the bag laundry where they were stored until ready for treatment. The bags were of heavy cloth and too valuable to be destroyed. Moreover, approximately 2 lbs. of niter adhered to the inside of each bag, making a salvaging process distinctly worth while. The bags were first put in a bag shaking drum which loosened all large lumps of niter. The niter thus removed was put through a rotary screen which separated the bag ravelings from the niter. The lumps were then trucked back to the niter storage house. The bags were given one or two washings with steam heated water, in dipping tanks, all remaining niter being washed out and dissolved. The bags were then dried, first in a centrifugal extractor and then in steam dry room. The water from the washpans was evaporated and the nitrate of soda finally crystallized out. The storage house consisted of concrete bins housed over by a steel frame building, each house, of which there were two, serving two banks of retorts and having a capacity of 585,600 cu. ft.

Handling of nitrate from storage was accomplished by a Telpher system. The Telpher delivered to the dryers which were arranged in batteries of three, one battery to each unit or bank of retorts. These dryers were slowly rotating, steel cylinders, 4 ft. in internal diameter and 30 ft. long, heated by gas flame through a brick furnace or combustion chamber placed at the discharge end of the dryer. This chamber was 6 ft. 3 in. in width, 10 ft. long, and 8 ft. 4 in. high.

From the dryer the nitrate dropped through a chute to a conveyor serving three dryers, which, in turn, fed an elevator delivering to the dry nitrate overhead bin.

Under each dry nitrate bin were two scale hoppers, fed by gravity, in which the retort charge was weighed. The scale hopper delivered by gravity to the retort charging crane, which traveled on a runway directly over the retorts and was operated by cables.

As mentioned above, there was a total of ninety-six retorts arranged in banks or units of twenty-four each. These retorts were cylindrical with hemispherical bottoms, and were 8 ft. in inside diameter and 9 ft. 8.5 in. deep. They were fitted with a cover having the necessary openings for the introduction of nitrate and acid and for the escape of the fume.

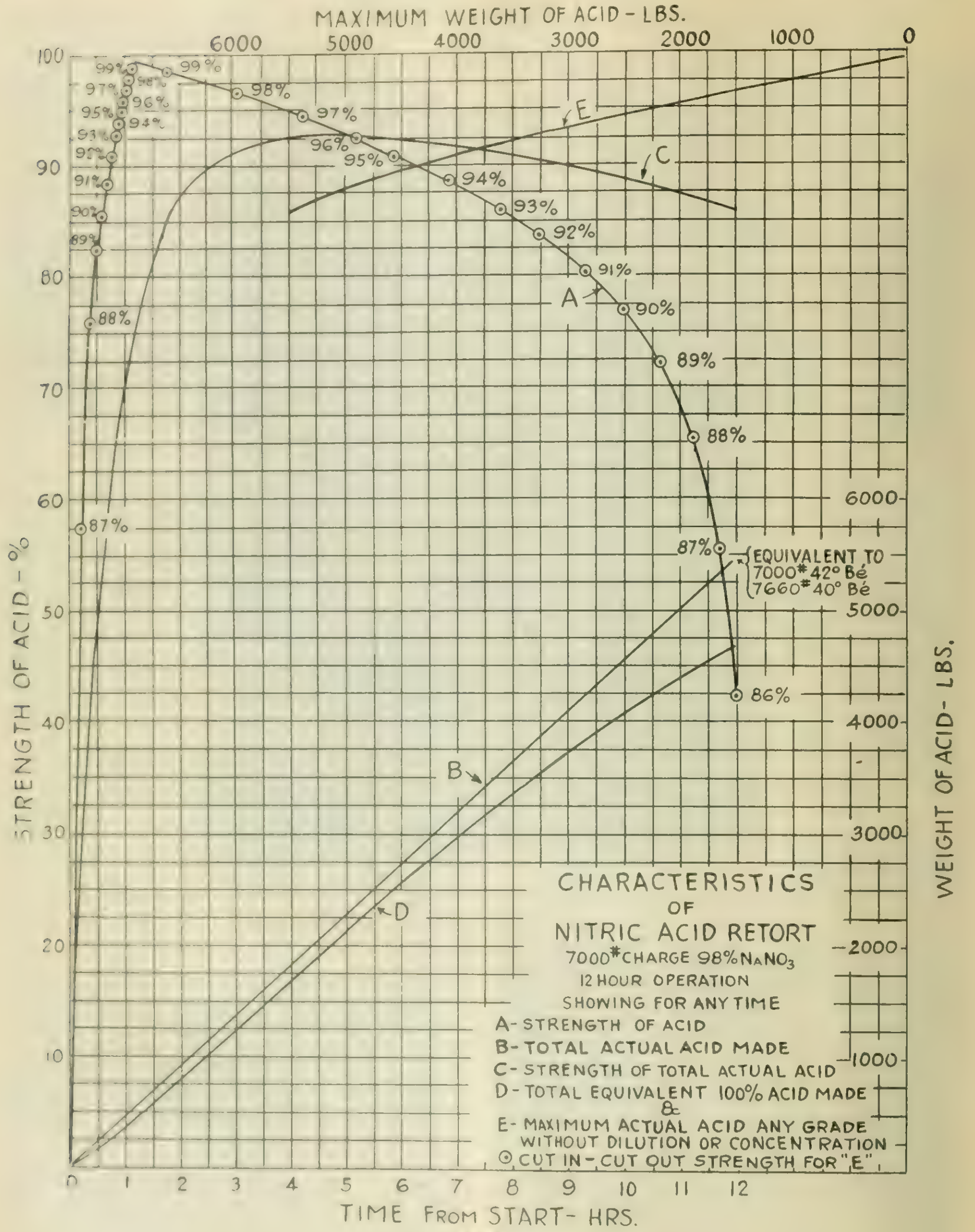

Fig. 7

In charging, the nitrate was dumped in first, the standard charge being 7000 lbs., and an approximately equal amount of 66° Bé. sulfuric acid was run in. The cooking-off period occupied from 8 to 11 hrs., so that two charges per 24 hrs. were possible. The maximum heat desired was 250° C.

After cooking-off, the residual niter cake was tapped out of an opening in the bottom of the retort and flowed into a flume, running the entire length of the retort house, through which water was running continuously. As no use was to be made of this cake the flume delivered to the sewer.

The gas leaving the retorts passed through an 8-in. acid-proof iron pipe, insulated against heat loss by a covering of asbestos, into the bleach pot. The latter was a small acid-proof iron pot packed with spiral acid-proof pottery rings. In this bleach pot a small amount of nitric acid was condensed and run off at the bottom through a 3-in. line. The remainder of the fume passed upward through the ring packing and into the condensers proper. Each condenser consisted of nine 6-in. acid-proof iron pipes comprising nine lengths of pipe 5 ft. long, connected at the ends by return bend fittings so as to form a continuous vertical coil 6 ft. wide and 8 ft. high. These were sprayed by cooling water on the outside for condensation of the fume to nitric acid. The pipes comprising the condenser were inclined in such a way that all acid condensed ran off through the bleach pot, where the action of the hot gases drove off the lower oxides of nitrogen brought down in the condensation, resulting in the bleaching or lightening in color of the product. The remainder of the gas, consisting of residual air in the retort and all lower oxides of nitrogen, passed from the condenser through tile lines into hyponitric towers. The latter, of which there were eighteen to each unit arranged in two parallel lines of nine towers each, consisted of 30-in. chemical stoneware sections resting in acid-proof iron dishes (Fig. 1).

There were six tower sections to each tower and all were packed with spiral chemical rings. The flow of gas was in series through these towers. Water was started from the top of Tower 18 and was pumped over each tower in turn in series, countercurrent to the flow gas. In this countercurrent circulation the water gradually adsorbed the acid in the gases, coming off at Tower 1 as weak nitric acid. The gases leaving Tower 18 escaped to the atmosphere practically free of nitric acid.

The acid from the condensers and bleach pots flowed through acid coolers, which consisted of loops of 2-in. acid-proof iron pipe immersed in a trough of water, and from the coolers passed directly into the mixing tanks.

Each unit was provided with three mixing tanks, of steel plate construction, 8 ft. in inside diameter, 30 ft. long, and with a 2-in. lining of acid-proof radial brick. These tanks were so connected that each could draw oleum from the oleum tank, weak nitric acid from the weak acid tanks, or strong acid direct from the strong acid lines.

In mixing, the proper amount of oleum from the oleum storage tank was led into the mixing tank and followed by weak or strong nitric acid in the proportions necessary to give the mix desired. The mixing tanks were provided with motor-driven agitators in order to provide a uniformly mixed product, and there was also provided a circulating pump which drew the acid from the tank through a cooler and returned it to the same tank. This acid cooler consisted of a coil of five lengths of 6-in. acid-resisting iron pipe sprayed with water.

During the period of operation there was an average of 7200 lbs. of nitrate per retort charge. It was found that, after the difficulties always incident to the starting of a new plant were overcome, it was possible to get about two and one-half charges per retort per 24-hr. day, and, had the plant continued to run on this schedule, could doubtless have been kept up with such retorts as were in operation.

Including the starting-up period, the yield of nitric acid per 100 lbs. of sodium nitrate was approximately 65 lbs. The sulfuric acid ratio to sodium nitrate was slightly less than 1 : 1.

Short Method for the Ultimate Analysis of Coal[1]

By S. W. Parr

University of Illinois, Urbana, Illinois

FOR purposes of the engineer in boiler testing, the following method for determining the carbon, hydrogen, and oxygen in coals has been in practical use for a number of years with very satisfactory results.

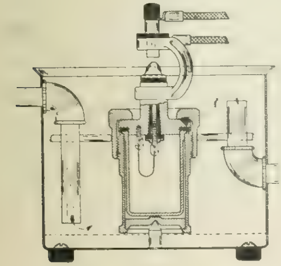

Fig. 1

Fig. 2

An ordinary combustion of the coal is made with sodium peroxide by use of the calorimetric bomb or similar devices, especially adapted to total carbon or sulfur determination, as shown in Figs. 1 or 2. The carbonate formed is discharged in any apparatus suitable for accurately measuring the carbon dioxide as shown in Fig. 3.

Having now the values in hand for sulfur and B. t. u., the calculations are of a simple order.

ULTIMATE ANALYSIS OF COAL

MOISTURE FREE

1. Weight of sulfur × 2777 = Calories from sulfur as FeS_2.
2. Weight of carbon × 8080 = Calories from carbon.
3. Total determined calories − (1 + 2) = Calories from available hydrogen.
4. $\frac{\text{Calories from available hydrogen}}{34{,}450} =$ Weight of available hydrogen.
5. Nitrogen present may be assumed as a constant of 1.25 per cent.
6. Then, by difference, 100 − (S + C + H + N + ash as weighed) = (O + H).[2]
7. 8/9 (O + H) = Total oxygen.
8. 1/9 (O + H) = Combined hydrogen.
9. Then, combined hydrogen + available hydrogen (8 + 4) = Total hydrogen.

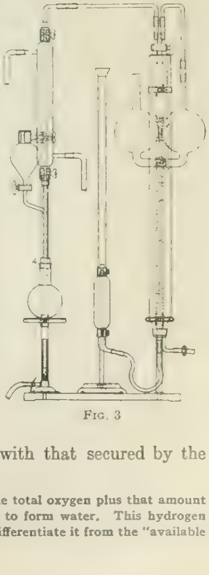

Fig. 3

By deriving the factors as thus indicated, we have all of the constituents as obtained by ultimate analysis and with a degree of accuracy entirely commensurate with that secured by the longer process.

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[1] Presented before the Division of Industrial and Engineering Chemistry at the 63rd Meeting of the American Chemical Society, Birmingham, Ala., April 3 to 7, 1922.

[2] The expression (O + H) refers to the total oxygen plus that amount of hydrogen necessary to combine with it to form water. This hydrogen is referred to as "combined hydrogen" to differentiate it from the "available hydrogen."

The Mechanism of Lubrication—I[1]

(ABSTRACT)

By Robert E. Wilson[2] and Daniel P. Barnard, 4th

[illegible] Applied Chemistry, Massachusetts Institute of Technology, Cambridge, Mass.

Although a large number of investigators have published data bearing on the subject of lubrication, the wide variations in their operating conditions have thus far prevented any satisfactory correlation of their results, or the establishment of definite conclusions as to the [illegible] as the smoothness and clearance of the bearing, the "oiliness" of the lubricant, etc.

The basic difficulty lies in the fact that f, the coefficient of friction, is, in the case of a journal bearing, some unknown function of at least nine variables—z, n, p, c, d, l, S, M, and O, where

z = Viscosity of the lubricant *at the operating temperature.*
n = Revolutions per minute.
p = Pressure on bearing.
c = Diametral clearance of bearing.
d = Diameter of journal.
l = Length of bearing.
S = Surface conditions (kind of metal, smoothness, etc.).
M = Method (and amount) of oiling.
O = "Oiliness" factor of the lubricant.

However, making use of dimensional reasoning as first suggested by Hersey,[3] it can be shown that f, a factor without dimensions, cannot be an *independent* function of all these variables, but only of their *combination* in such forms that all dimensions are canceled out. We may therefore write:

$$f = \phi\left(\frac{zn}{p}, \frac{c}{d}, \frac{l}{d}, \text{S, M, O}\right)$$

of which only the first two are important or primary variables, and indeed the first one includes the only three important variables involved in making tests on a given bearing under [illegible].

If, then, all the observed values of f obtained on a given bearing by varying the load, speed, and viscosity of lubricant, are plotted against the modulus zn/p, they should approximate a line which represents the unknown functional relationship. For the *ideal* case of a centrally operating bearing with perfectly smooth surfaces, no end leakage, etc., this function would be represented by a straight line passing through the origin, with a slope inversely proportional to the ratio c/d. For actual bearings this simple relationship would certainly not hold, but the shape and location of the curve which best represents the observed results should give valuable information as to the effect and importance of the other, or secondary variables [illegible].

All the published results which contained adequate data have been plotted on a large scale by the above-recommended method, and most of the plots are reproduced in the original article. Within the limits of this abstract it is possible to show only a typical curve, based on the results of Stribeck, using two kinds of bearing metal.

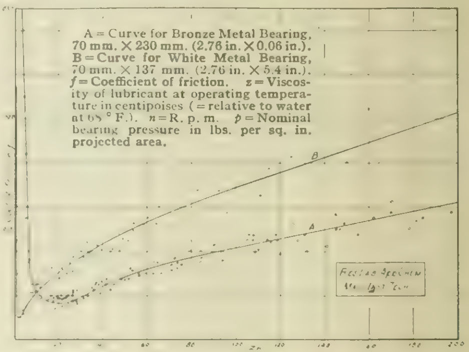
Each of these curves [illegible] made up of two [illegible] as follows:

1—The right-hand portion, which is the region of perfect fluid film lubrication, in which the friction coefficient is roughly proportional to zn/p.

2—The critical point of minimum friction where the speed or viscosity becomes so low, or the pressure so high, that the fluid film begins to rupture.

3—The sharply rising portion of the curve to the left of the critical point, which is the region of partial lubrication, in which there is increasing friction, metal to metal contact, and abrasion, as zn/p decreases below its critical value.

Many of the contradictory statements in the literature are due to failure to realize in which of these regions a given set of experiments were being conducted.



Results Obtained by Plotting Observed Values of f against zn/p for Two Different Bearings

The design of bearings and selection of lubricants may now become a definitely calculable matter. Bearings should not be designed to operate precisely at the point of minimum friction, because any momentary decrease in zn/p would carry them into the unstable region of partial lubrication, where serious abrasion and overheating are certain to result unless the journal is stopped. The *safe average operating value* of zn/p should therefore be obtained by multiplying the value of zn/p at the critical point by a suitable factor of safety—say around 5—depending upon the degree of variability of the service conditions. The problem is then merely to adjust the size of the bearing and the viscosity of the lubricant to give the desired value of zn/p.

The importance of the precise location of the critical point should be emphasized. For example, in the figure the casual observer would consider that Bearing A was the better because it gave the lower coefficients of friction over most of the normal operating range; but actually its critical point is so much higher than that of B that its value of f under *safe operating conditions* (factor of safety = 5) is *twice* that of B. In spite, however, of the great importance of the critical point, very little experimental work has ever been done to determine the effect of various factors on its location.

The more important *tentative* conclusions drawn from a careful study of the available data may be summarized as follows:

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[1] [illegible] 1922 [illegible]

[2] [illegible]

[3] [illegible]

(A) In the Region of Fluid Film Lubrication:

1—f is a function of zn/p, as demanded by dimensional reasoning.

2—The "oiliness" of the lubricant has no effect.

3—The nature of the bearing metal has no effect.

4—The method of oiling has no effect, providing *enough* is supplied to keep the bearing *full*.

5—Oil grooves in the pressure side of the bearing tend to give abnormally high values of f in the operating range of zn/p.

6—The curves are higher for low clearance ratios, but the effect of clearance is not as great, especially at larger clearances, as would be calculated.

(B) The Location of the Critical Point Is:

1—The most important single factor in determining the efficiency of a bearing.

2—Lowered by small clearance ratios.

3—Lowered by greater smoothness of the surface.

4—Lowered by the oiliness of the lubricant.

5—Affected by the nature of the bearing metal.

(C) In the Region of Partial Lubrication:

1—The oiliness of the lubricant is much more important than its viscosity.

2—The nature of the metal plays an important part.

3—f is not necessarily a function of zn/p because high loads may change the character of the *bearing surface* by squeezing out an adsorbed film.

In view of A-2, it is obvious that the average "oil-testing" machine, operating as it does in the region of fluid film lubrication, is nothing but a *very crude* type of *viscosimeter*, and gives no information as to the oiliness of a lubricant. To obtain data of real value regarding oiliness, experimentation must be focused on the region of *partial* lubrication and especially on the critical point of film rupture, in spite of the recognized difficulties involved. These matters are discussed more in detail in the following paper.

The recommended method of treatment is shown to be of much practical value in diagnosing and solving practical lubrication problems.

The Mechanism of Lubrication—II[1,2,3]

Methods of Measuring the Property of Oiliness

By Robert E. Wilson[4] and Daniel P. Barnard, 4th

Research Laboratory of Applied Chemistry, Massachusetts Institute of Technology, Cambridge, Mass.

"Oiliness" is defined as that property of lubricants by virtue of which one fluid gives lower coefficients of friction (generally at slow speeds or high loads) than another fluid of the same viscosity. Its importance under practical operating conditions is shown to be greater than is generally recognized. Unfortunately, however, no satisfactory method has ever been developed for the quantitative measurement of this property in comparing different lubricants.

This paper describes the variety of possible methods of measuring the property of oiliness and of throwing light on the mechanism of partial lubrication, including (1) the use of a Deeley type machine to measure coefficients of friction between plane surfaces at slow speeds; (2) a refined and reproducible method of determining static coefficients of friction between partially lubricated metal surfaces; (3) the measurement of the interfacial energy between oil and mercury; (4) measurements of the electrical resistance and the rate of formation of adsorbed films on metal surfaces; and (5) the clogging of fine metal capillaries through which lubricants are forced. Some other interesting preliminary experiments are also described.

In the light of the results obtained by the above-mentioned methods, it is believed that the static friction test with proper refinements is the best single measure of the properties of oiliness, but that it should be supplemented by measurements of the thickness of the adsorbed films at high pressures, in order to throw more light on the mechanism of the action of different constituents in lubricating oils.

Animal and vegetable oils are almost invariably superior in oiliness to straight mineral oils. The blending of considerable proportions of these neutral glycerides with mineral oils greatly improves their oiliness, but the same results may be accomplished by adding much smaller proportions of other materials, such as fatty acids or oil-soluble soaps.

These experiments entirely confirm the customary hypothesis that oiliness is due to selective adsorption of constituents in the oil by the metal surface, but the common conception of a monomolecular adsorbed film which acts merely by masking the attractive forces of the metal surfaces for one another appears to be incorrect. The adsorbed film is shown to be of colloidal rather than molecular dimensions, is a plastic solid rather than a fluid film, and apparently acts by smoothing over surface irregularities, carrying much of the load, and minimizing metal to metal contact and abrasion. The structure and physical characteristics of this film seem to be more important than its thickness in determining its efficiency in lowering friction.

The constituents of lubricants which form these adsorbed layers may be selectively adsorbed and largely removed from the oil by repeated treatments with very finely divided metals, such as iron-by-hydrogen.

In THEIR previous article the writers have shown that under certain adverse conditions—especially at slow speeds and high loads, or where the oil supply is inadequate—a perfect fluid lubricating film cannot be maintained, and lubrication of the rubbing surfaces depends on the ability of a very thin, probably semisolid, film of lubricant to adhere to the metal surfaces in spite of the pressure tending to squeeze it out and the abrading effect due to motion. This fundamental property of "oiliness," which is possessed to variable degrees by all good lubricants, has been the subject of a considerable amount of investigation, chiefly in England, but although there is considerable evidence to indicate the presence of some such absorbed film, its composition, structure, thickness, and the mechanism of its formation are

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[1] This covers the second part of a paper presented by the writers at the January meeting of the Society of Automotive Engineers and at a meeting of the Delaware Section of the American Chemical Society in February 1922. The first portion is abstracted on page 682 and should be read before this.

[2] Published by permission of the *Journal of the Society of Automotive Engineers*.

[3] Published as Contribution No. 48 from the Research Laboratory of Applied Chemistry, Massachusetts Institute of Technology.

[4] Director, Research Laboratory of Applied Chemistry, M. I. T.

matters which still remain to be established. Furthermore, [illegible] of the property [illegible].

For the purposes under discussion, the "oiliness" of a lubricant will be defined as the property by virtue of which one fluid gives lower coefficients of friction (generally at slow speeds or high loads) than another fluid of the same viscosity.

One reason why the property of oiliness has not received the attention it appears to deserve lies in the fact discussed in the previous paper, namely, that practically all well-designed journal bearings operate for at least 95 per cent of the time under conditions of perfect fluid film lubrication, where the oiliness of the lubricant plays no part. As a result, many are inclined to question the practical value of a detailed consideration of the more exceptional and complicated case of *partial* lubrication where the speed is too low or the load too high to maintain the normal fluid film between the metal surfaces, and the property of oiliness becomes important. Since this point of view is frequently taken by experienced lubrication engineers, it seems desirable to point out the following basic reasons why the laws of partial lubrication and the property of oiliness are of very real practical importance, apart from their theoretical interest.

1—Every bearing must occasionally start and stop, and thus pass through the region of partial lubrication, where the friction coefficients are enormously higher than at normal speeds and some abrasion is certain to result. The resultant roughening of the bearing surfaces is directly or indirectly responsible for a large proportion of bearing failures, although the actual failure may take place only after the bearing has been running for some time at high speeds, when the rough surface causes overheating. By using a lubricant of high oiliness which will maintain a film even when the bearing is not rotating, it is possible to minimize this abrasion and its resultant effects.

2—Conditions very frequently occur, especially in machinery in the hands of unskilled operators (under which head we may include most automobiles!) where the oil supply is temporarily deficient for one reason or another. Under these conditions the only protection of the bearing is a tenaciously adsorbed film of lubricant which will remain for a long time and prevent seizing and damage to the bearing, even though it gives a higher coefficient than that of the fluid film which should be present.

3—In many cases, such as the piston rings in an engine cylinder, or the crosshead of the steam engine, there is a reciprocating motion [illegible] and under these conditions the maintenance of a perfect fluid film, especially at the ends of the stroke, is very difficult, and the amount of friction depends very largely on the permanence and lubricating value of the adsorbed film. The precise type of lubrication in the cylinders is, to be sure, not so important in many of the more poorly made engines where, to quote a well-known contemporary, "the threads on the piston rings do not fit those in the cylinder."

4—There are many special uses of lubricants where high pressures [illegible] are absolutely essential, [illegible] adsorbed film can pre[illegible]. Important examples under this head [illegible] where greases are usually employed in [illegible] cutting or threading most metals, where lard oil is unquestionably superior to ordinary mineral oils.

5—From the standpoint of the producer of lubricants, a study of the film-forming tendency of oils appears to be indispensable, since this unmeasured oiliness factor is the only fundamental [illegible] good lubricants, poor lubricants, and so-[illegible]. Under these [illegible] it is surprising that neither the producers nor the consumers of oils have developed any recognized test or specification to tell the difference between the amount of oiliness possessed by different lubricants (even though such tests might hamper [illegible]).

6—Probably the most important way in which the property of oiliness affects the [illegible] all bearings [illegible] of perfect fluid film lubrication, has apparently never been pointed out. This is the influence which the property of oiliness has on bearing design.

As has been shown in the previous article, bearings are designed primarily to operate in the range of perfect fluid film lubrication and reasonably near to the point of minimum friction. Unfortunately, it is not possible to operate exactly at this point because it is just on the verge of the dangerous condition of partial lubrication. It is therefore necessary to multiply the value of $\frac{zn}{p}$ at the critical point by a factor of safety of, say, 5 to determine the safe operating value, though these conditions give much higher coefficients of friction than the minimum value.

The effect of the oiliness of the lubricant on this matter of design is apparently twofold: first, it lowers to a considerable extent the critical point;[5] and second, it decreases the danger attendant upon operating occasionally in the region of partial lubrication. It is therefore quite reasonable to use a smaller factor of safety if a lubricant with a high degree of oiliness is assured. In other words, a bearing supplied with a very oily lubricant could be designed to operate at a value of $\frac{zn}{p}$ determined by multiplying a *lower critical value* by a *lower factor of safety*, thus giving a *much* lower operating coefficient of friction than if reliance could not be placed on the degree of oiliness possessed by the lubricant.

In view of the foregoing facts, this Laboratory believes that the whole question of oiliness and the mechanism of lubrication at low speeds is the most important present problem in the entire field of lubrication, from both a practical and a theoretical standpoint. As the first point of attack upon the problem, the Laboratory has been endeavoring for some time to work out satisfactory methods of measuring this oiliness factor, and has also been conducting experiments designed to throw light on the mechanism by which the film is formed. This work has for some time been subsidized by the General Motors Research Corporation, and more recently by the Standard Oil Co. (New Jersey), with whose kind permission this article is published.

In this preliminary investigation of the factor of oiliness the writers offer no apology for the fact that they have not as yet attempted to simulate actual working conditions in bearings, etc. As has already been pointed out, the factors which determine the coefficient of friction in a bearing are many and difficultly separable. Theoretically, under certain conditions a bearing could be used to measure the *viscosity* of a lubricant; practically, the only way to obtain a satisfactory degree of accuracy is to use a viscosimeter which bears no resemblance to a bearing; similarly, in developing the quantitative measure of *oiliness* it is desirable to go to extreme conditions and eliminate all other factors as far as possible. It is also the belief of the writers that in the present preliminary stage of the work, undue reliance should not be placed on any single supposed test of the oiliness factor, but that several radically different methods of measurement should be tried to determine which results are most uniformly consistent with the known properties of the oil and its behavior in actual service tests in bearings operating under conditions of partial lubrication. This comparison of the results obtained by different methods of testing should also aid greatly in explaining the mechanism of partial lubrication.

Thus far the writers have made use of six independent methods of measuring some property connected with the adsorbed lubricating film on metal surfaces, not to mention several others which have been tried out and discarded for various reasons. The results of these preliminary studies are admittedly inconclusive in many important details, but a number of new and interesting facts have been brought to light and it is hoped that a detailed presentation of the methods used may stimulate discussion and research in this important field.

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[5] As indicated in the preceding article, insufficient work has been done to settle this point definitely.

In view of the specified definition of oiliness in terms of the coefficients of friction for partially lubricated surfaces, measurements of the coefficient of friction under conditions which emphasize the effect of oiliness is the obvious first approach to a solution of the problem. This means that the measurements should be made in the region of partial lubrication, by using either very low speeds or high pressures.

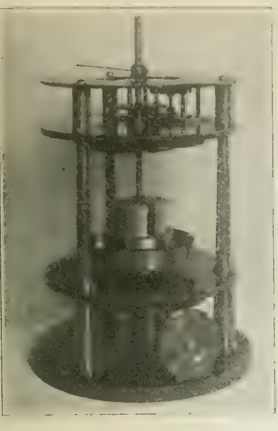

Fig. 1

In undertaking such a study it is well to recognize at the outset one very serious and apparently inescapable difficulty which besets any method of measuring friction under conditions of partial lubrication. This difficulty is due to the combination of two facts: first, in this region the nature and condition of the surfaces profoundly influence the coefficient of friction; and second, some abrasion is certain to result if the test is severe enough to distinguish clearly between good and bad lubricants. It is therefore necessary to use extreme care in the preparation of the surfaces if reproducible results are to be secured, and the surfaces must be refinished and brought back to their original condition after virtually every test. As a result, the time spent in lapping and repolishing surfaces is generally a matter of days, as compared with minutes required for making the actual friction measurements. This results in slow progress, especially in the early stages of a fundamental investigation where the relative importance of the various factors and the proper methods for obtaining the best results are not yet established. This difficulty is even more pronounced in working with journal bearings because any repolishing or scraping tends to increase the clearance and change the whole behavior of the bearing. The use of flat bearing surfaces for such tests is therefore decidedly advantageous.

Results on a Deeley Type Friction Machine

The most promising method described in the literature for studying the mechanism of partial lubrication at slow speeds and comparatively high loads is the Deeley type of machine.[6] Apparently only one of these machines has previously been constructed, that by Mr. Deeley himself, and the meager amount of data secured was insufficient to permit the formulation of important conclusions.

The construction of the Deeley type machine used by this Laboratory is shown in Figs. 1 and 2. It consists essentially of a flat plate which can be rotated at any desired (slow) speed, on which rests a disk supported by three pegs and pressed down by weights of any desired size. The disk is held in place by a small vertical shaft which is free to turn except for the restraint imposed by a calibrated spiral spring. When the bottom plate is rotated at constant speed the top disk follows it until the spring overcomes the frictional resistance and slipping begins. The first maximum reading on the graduated scale measures the static coefficient of friction, and the steady position which it assumes as rotation is continued is a measure of the kinetic coefficient at the speed in question. A damping device is added to prevent too violent oscillations of the system when the disk first breaks away.

The general procedure in making measurements is as follows: When glass surfaces are used they are first cleaned by washing with soap and water and then with chromic acid. They are next rinsed thoroughly with distilled water and dried on a clean cotton towel. They are then placed on the machine, the receiver filled with oil, covering the bottom plate to a depth of 1/16 in. and the machine run at high speed and light load for several minutes in order to rid the surfaces of any adhering moisture film. In making a series of readings the machine is adjusted to the speed required, the load is applied, and as soon as the pointer comes to rest the reading is noted and the machine stopped. In this way undue abrasion is prevented, as the pointer almost always comes to rest after one or two revolutions of the turntable. By the time that a half a dozen readings can be taken, however, the surfaces are so badly scored that it is necessary to refinish them before they may be used again. This rapid wear affects the results considerably, but thus far no way has been found of avoiding it. For this reason the values given below must be considered only approximate.

In using metal surfaces the procedure followed is somewhat different. The plate used consists of a casehardened tool steel disk, which after hardening is ground true and polished. The tripod is made of cast iron and has rectangular feet, approximately 1/4 in. by 1/16 in. They are so placed that the longer dimension is at right angles to the path of travel. These surfaces are ground together first with carborundum flour and then run dry for several days until both surfaces are bright and smooth. They are next oiled and run in for about 50 hrs. more. Following this treatment the surfaces are removed from the machine, carefully cleaned, and oiled with the oil to be tested, and the machine run till constant readings are obtained. This is frequently a period of 8 to 10 hrs.

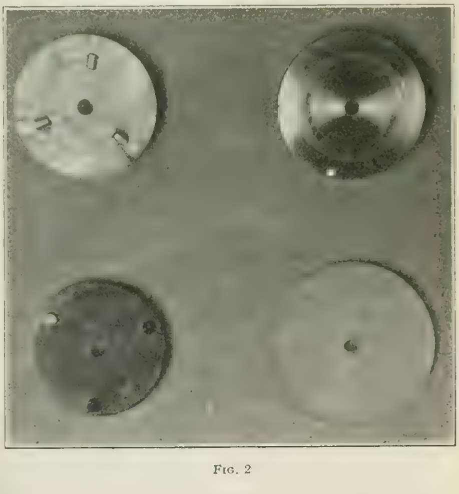

Fig. 2

One of the principal questions which it was hoped to settle by the use of the Deeley machine was whether the coefficient of friction drops off steadily with increasing speed, or whether it first rises from the static value and passes through a maximum at very slow speeds. A statement of the latter effect is made by Archbutt and Deeley[7] and repeated by several other recent writers on the subject, but the experimental data on which it is based seem to be extremely meager,[8] and in view of the difficulty of obtaining reliable results under conditions of partial lubrication it was felt desirable to check up this statement which seems contrary to both theory and general experience. It was also felt that a study of the static coefficient and the kinetic coefficient at slow speeds would throw considerable light on the best conditions under which to obtain a quantitative measure of the property of oiliness.

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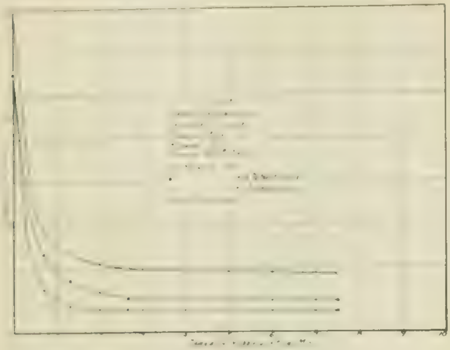
[6] The Deeley machine and its use are described in some detail in the 1920 Report of the Lubricants and Lubrication Committee of the British Department of Scientific and Industrial Research.



Using the above-described machine, an extensive series of observations have been made to determine primarily the effect of varying speed on the coefficient of friction under conditions of partial lubrication. Typical sets of results are shown in Figs. 3 to 6, inclusive. In making these tests an effort is made to distinguish between animal or vegetable oils, most of which are known to possess the property of oiliness to a high degree, and straight refined mineral oils of similar viscosity, of which Velocite B, made by the Vacuum Oil Co., is fairly typical. It was also desired to check up the observations of Archbutt and Deeley on the effect of adding small amounts of fatty acids to the mineral oil.

Fig. 3 shows some of the results which were obtained with this machine using rubbing surfaces of glass, and brings out clearly the effect on the coefficient of friction of adding small amounts of fatty constituents to a high-grade, paraffin base spindle oil. It is noted that over the entire range of rubbing speeds covered, from static up to 8 ft. per min., the oils containing 5 per cent neutral lard oil and 1 per cent stearic acid gave much lower values for the coefficient than did the straight mineral oil. One per cent of stearic acid serves to lower the coefficient even more than does 5 per cent of the neutral animal oil.

The values shown for the static coefficient are undoubtedly inaccurate, on account of the great tendency of the well-cleaned glass surfaces to seize and give quite variable results. Glass also does not appear to adsorb a film from ordinary lubricants at all firmly, and hence it gives a very high static coefficient. The glass surfaces used in these tests all showed very deep scratches after one or two readings had been obtained. The very rapid drop in the coefficients as soon as appreciable speeds are reached is also consistent with what might be expected from such plane, highly polished surfaces, which would require only a very thin fluid film to prevent all solid contact.

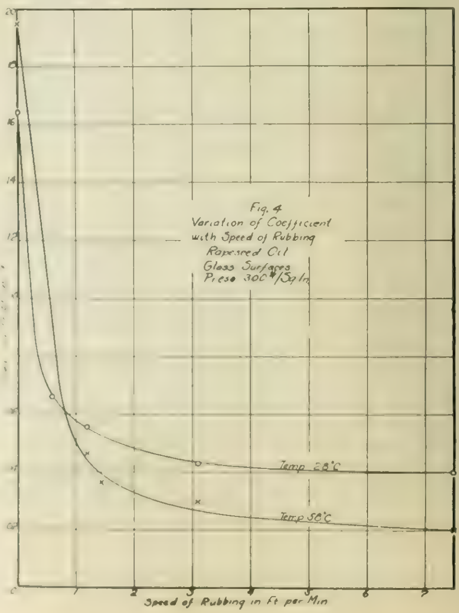
Fig. 4 shows the variation of the coefficient with speed of rubbing for a given oil, rapeseed, at two different temperatures. It is interesting to note that at low speeds the higher temperature gives the higher coefficient, while at speeds above 1 ft. per min. the two curves reverse their relative positions. This is readily explainable on the basis of the fact that adsorption is the main factor in reducing the coefficient at lower speeds, and this is always more pronounced at lower temperatures, whereas at higher speeds the viscosity of the fluid is the primary factor in determining the friction, and this is lower at the higher temperature.

In Fig. 5 is shown the effect of adding small amounts of stearic acid to the mineral oil, using cast iron *vs.* steel surfaces. The presence of but 0.5 per cent of the fatty acid apparently lowers the coefficient to less than one-half of its former value in the range studied. Increasing the fatty acid content to 2 per cent effects a further, though less marked, reduction. The relatively enormous effect of such small additions can apparently be explained only on the assumption that the fatty acid is *concentrated* in a surface film by a selective adsorptive force at the metal surface.

The curves again show a steady decrease from static friction with increasing speed of rubbing, the drop being, however, much less precipitous than for glass surfaces.

The next chart, Fig. 6, compares the results on blown rapeseed oil, mineral oil, and mineral oil plus 2 per cent oleic acid. The oleic acid appears slightly superior to the stearic acid as an adulterant after motion has started, though the static coefficient is somewhat higher. The straight blown rapeseed gives only slightly lower values than the mineral oil plus oleic acid.

It is impossible within the scope of the paper to present all of the rather extensive experimental results secured on this machine. For example, several series of tests were made to determine the effect of load on the coefficient at speeds up to 8 ft. per min., and with pressures varying from 25 to 140 lbs.



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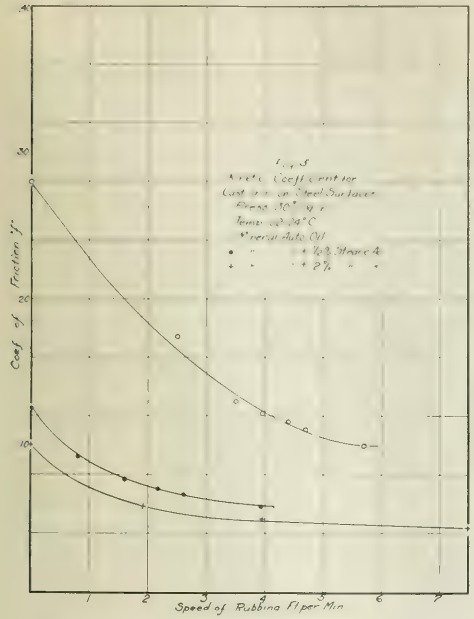
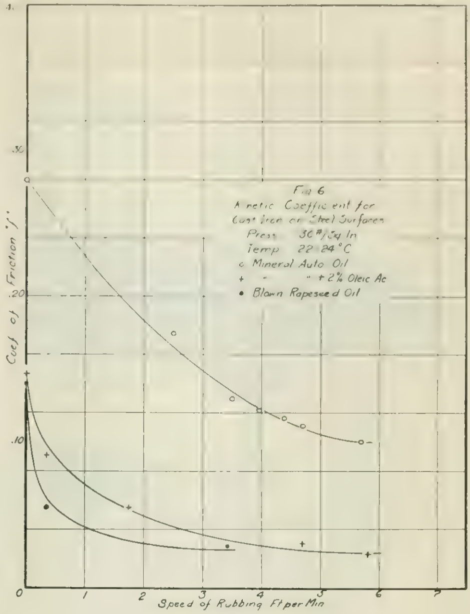
[7] [illegible]

[8] [illegible] 1877, 8

per sq. in. The curves for different loads were practically identical in shape and fairly close to one another in position. The relative positions of the curves for different loads were not always consistent, but in general the lower loads tended to give slightly lower coefficients at moderate speeds, though most of the differences were not much greater than the experimental error of duplicate runs. Additional measurements were made of the *static* coefficient at loads up to 1600 lbs. per sq. in., without noting any consistent variations, though the average deviation of duplicate measurements at the higher loads was about 15 per cent.





As a result of the work on the Deeley type machine the following conclusions may be drawn as to the friction between *plane surfaces* at *slow speeds:*

1—There is no maximum coefficient of friction at very slow speeds, the static coefficient always being higher than any kinetic coefficient.

2—For polished glass surfaces the drop from the static coefficient to the slow speed kinetic is extremely sharp and it is doubtful if the curves should really be considered as continuous. On metal surfaces, however, the static coefficients are not so high and are more reproducible, and the curves appear to be continuous, the static coefficient being only slightly higher than those at very slow speeds.

3—Within wide limits pressure has comparatively little effect on the *coefficient* of friction under the above-specified conditions.

4—Animal and vegetable oils show consistently lower coefficients than ordinary refined mineral oils.

5—The addition of very small amounts of fatty acids, or of considerably larger amounts of neutral vegetable oils, to mineral oils produces a very marked lowering of the coefficient of friction, thus confirming the statements of Southcombe and Wells.

6—On metal surfaces the maximum differences in the coefficients of friction for different oils are found in the neighborhood of zero velocity. In other words, the *static* coefficient of friction would appear to be the best single measure of the oiliness factor of a lubricant, especially considering the greater simplicity of the measurements. Slightly greater *percentage* differences, and greater reproducibility, may be obtained at speeds in the neighborhood of 0.5 ft. per min., but such conditions would require more complicated apparatus and cause much more abrasion than would the determination of the static coefficient.

7—All of the above data confirm the belief that the oiliness factor of lubricants is due to a tenaciously adsorbed film of some constituent of the lubricant, the presence of which diminishes or prevents metal to metal contact, even after the surfaces have been pressed together for some time. This ability of the film to withstand prolonged pressure without being squeezed out indicates that it partakes of the nature of a plastic solid[9] with a fairly high yield point, rather than being a fluid film such as does the lubricating in a rapidly rotating bearing. In order to account for its remarkable effectiveness, even on surfaces with very appreciable irregularities, this film would apparently have to be much thicker than the mere monomolecular film which is frequently postulated.

DEVELOPMENT OF A METHOD OF MEASURING THE STATIC FRICTION COEFFICIENT

In view of the fact pointed out in the sixth conclusion just preceding, and of the time-consuming nature of measurements on the Deeley machine, it seemed highly advisable to develop a rapid and reproducible method of measuring the *static* coefficient of friction for a large number of oils, reserving the use of the Deeley type machine for making a more thorough study of the more promising possibilities as indicated by these static friction measurements. A considerable amount of the time has therefore been devoted to the development of such a test, which has proved more difficult than was anticipated, although a fairly satisfactory solution has now apparently been attained.

Some interesting work along these lines has already been done by Langmuir,[10] Hardy,[11] and Lord Rayleigh.[12] Lang-

[9] This belief was enunciated and some supporting data offered by one of the authors at the Rochester Meeting of the American Chemical Society, April 25 to 29, 1921. See *Chem. Met. Eng.*, **24** (1921), 825.

[10] "Surface Phenomena of Ore Flotation," *Trans. Faraday Soc.*, **15**, III (1920), 62.

[11] "Static Friction, II," *Phil. Mag.*, [6] **38** (1919), 32; **40** (1920), 201.

[12] "Notes on the Theory of Lubrication," *Ibid.*, **35** (1918), 157.

muir made measurements of the angle of slip between nonmetallic crystal surfaces, such as mica, quartz, galena, etc., in the presence and absence of monomolecular films of fatty acids, etc., while Hardy worked with various pure organic liquids on polished bismuth and glass surfaces and again obtained evidence of monomolecular adsorbed films. Lord Rayleigh made a few observations on glass surfaces. None of the sets of results are, however, readily applicable to the lubrication of metal surfaces with ordinary lubricants, though Hardy's methods of measuring the static coefficient were essentially those used in most of our measurements to date.

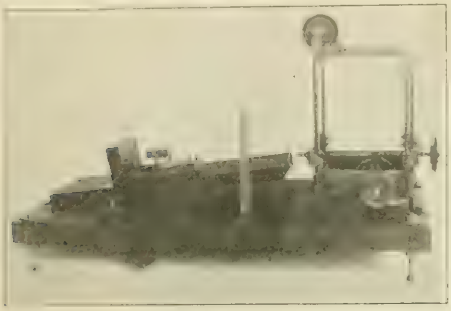


FIG. 7

In the initial experiments in this Laboratory attempts were made to determine the static coefficient between flat surfaces. The results obtained were entirely unsatisfactory owing to the practical impossibility of reproducing the original flatness of the surfaces and the size and shape of the area of contact. It was found necessary to obtain surfaces of as near perfect *smoothness* as possible, rather than working toward true flatness. True flats may be obtained only by lapping methods, and consequently always show many tiny scratches which are far more objectionable from the standpoint of accurate friction measurements than quite appreciable variations from precise flatness.

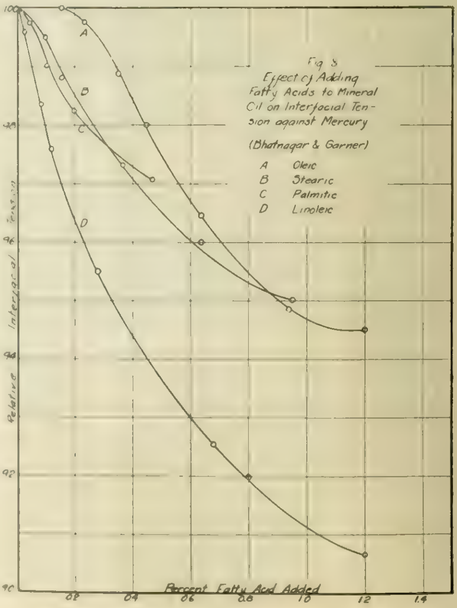
It might be argued that excessive smoothness would give results quite different from those obtained with the ordinary types of surfaces which are used in engineering practice, and such a possibility is indeed quite conceivable. As indicated previously, however, the primary need is for definite, reproducible measurements of the oiliness property; reproducible measurements require reproducible surfaces; if surfaces of a definite intermediate smoothness could be thus reproduced they might prove quite suitable for the purpose in hand, but no procedure to attain this end has yet been suggested, and the only alternative is to make the surfaces so extremely smooth that further changes in degree of smoothness would not affect the results. Furthermore, preliminary measurements with surfaces of intermediate degrees of roughness have shown that the order of magnitude and arrangement of results are nearly the same for all reasonable degrees of smoothness, but that the average deviation of the observations becomes less and less as the surfaces become smoother.

In order to avoid these serious difficulties, a modified method was developed which consists essentially in the measurement of the static coefficient (from the angle of slip) between two surfaces, one of which is a highly polished and approximately plane surface, while the other is a highly polished spherical segment with a definite radius of curvature (6 in.). By this expedient it is possible to focus all attention on the smoothness of the surface, while minor variations in the planeness or curvature of the surfaces have but little effect. Furthermore, the pressure per unit area is high without requiring the use of large weights, and is reproducible, although its exact magnitude is unknown. Fortunately, however, tenfold variations in the load (20 to 200 g.) have not been found to affect the results more than 3 or 4 per cent on the average.

To the uninitiated it may seem a fairly simple matter to produce surfaces which have a mirror-like smoothness and yet possess the other necessary properties. The most obvious method at first sight would be to electroplate the surfaces with some metal, such as gold, silver, or copper, which readily takes a high polish, but experiments with such surfaces indicate that even with comparatively small loads the surfaces are so soft that they are actually "ploughed" up whenever static friction measurements are made, and it was felt that the measurements were more a function of the internal properties of the soft metal film than of the adsorbed oil film. Other experiments with soft and readily burnishable metals lead to the conclusion that fairly hard materials must be used in order to obtain accurate and reproducible results.

One material, which takes a remarkably good polish, and yet possesses a high degree of hardness, is speculum metal, a definite crystalline compound of copper and tin in the proportions Cu_4Sn (68.2 per cent Cu, 31.8 per cent Sn). This metal is very brittle, but with proper care can be cast into the form of disks, hemispheres, or pegs which take an excellent polish. The metal also has the advantage of being practically noncorrodible.

In view of the probable specificity of different metals in building up an adsorbed film, it seemed desirable to approximate most service conditions by making at least one of the surfaces out of steel, preferably fairly hard. A great deal of difficulty was experienced in securing suitable pieces of steel which were free from microscopic inclusions of oxide or pits, and furthermore many steels can be ground to a very smooth surface and yet in the long polishing operation by cloth tend



to develop irregularities due to differences in hardness of different parts of the grain structure, or to form pits due to corrosion. In order to get a steel reasonably free from nonuniformities, recourse was had to the stock used in making micrometer checks, etc., or to the best quality of casehardened tool steel with very fine grain. The second difficulty (corrosion) has been overcome by using kerosene instead of water as the liquid on the polishing wheel.

The surfaces are prepared by lapping to the desired form, rough polishing with 60-min. carborundum on a canvas covered wheel, and finishing with levigated alumina on a wheel covered with a fine grade of broadcloth.

Static friction measurements have been made with various combinations of these two metals and also with Alloy 5, a low melting alloy (containing bismuth, tin, and cadmium), which it was found possible to cast in smooth hemispherical form on watch glasses, but which was too soft to give entirely satisfactory results. The best combination appears to be to make the spherical segment out of speculum metal and the plane surfaces of annealed high carbon steel, both being polished to a mirror-like smoothness. With such a combination of surfaces most of the abrasion comes on the steel, and twenty-five or thirty observations may be made before repolishing by moving the slider each time to a fresh part of the steel surface.

In measuring the static coefficient the plane surface is placed on a support, the angle of inclination of which can be slowly raised by a motor acting through a belt, light gears, and a cord and pulley to prevent the transmission of vibrations. The plane is flooded with oil, the curved slider placed in position on the plane, and the angle of inclination slowly increased until slip occurs. A stop is provided to prevent the slider from slipping more than about $^1/_8$ in. The surfaces are shown in position for a determination in Fig. 7, except that the spherical segment has been replaced by a tripod slider.

Table I shows the results of the preliminary experiments on four different combinations of surfaces with several typical oils which might be expected to differ in the property of oiliness. Each of the recorded results is an average of not less than ten, and generally about twenty, separate observations of the static friction coefficient. The average deviations varied from 2 per cent to 5 per cent, being generally below 4 per cent, so that the probable error of the average of twenty observations is generally less than 1 per cent as far as a particular set of surfaces is concerned. It has been found, however, that even in the case of the best combination thus far found (speculum *vs.* speculum), differences in the degree of polishing make perceptible differences in the results, even when a high degree of smoothness is apparently approached. Speculum *vs.* steel gives slightly greater deviations, but is recommended in order to approach more closely to service conditions. Too much reliance must therefore not be placed on the precise reproducibility of the different observations until further work has been done.

TABLE I—STATIC FRICTION MEASUREMENTS
INCLINED PLANE METHOD—SPHERICAL SEGMENT SLIDER
Load = 100 G.

	COEFFICIENT OF FRICTION		
OIL	Speculum on Steel	Speculum on Speculum	Alloy 5 on Steel
Glycerol	0.20	0.20	...
Velocite "B" Oil	0.182	0.173	0.152
Velocite "B" + 2% stearic acid	0.125	0.121	0.123
Velocite "B" + $^1/_2$% iron stearate	0.120	0.120	...
"Neutral" lard oil	0.125	0.126	0.093
Velocite "B" + 2% *p*-cresol	0.186	0.178	...
Velocite "B" treated twice with Fe by H	0.190	0.180	...

As to the significance of the typical results given in Table I, it will be noted in the first place that there is again a sharp distinction between lubricants, such as lard oil, which are known to possess a high degree of oiliness, and ordinary mineral oils; and also that small amounts of stearic acid added to mineral oils, such as Velocite B, give values which correspond very closely to the animal or vegetable oils. These results all check up remarkably well with the previously discussed results on the Deeley machine, except as to the precise magnitude of the static coefficients. It will be noted that ferric stearate is also very effective in lowering the coefficient, though the soap is rather unstable on standing in the mineral oil.

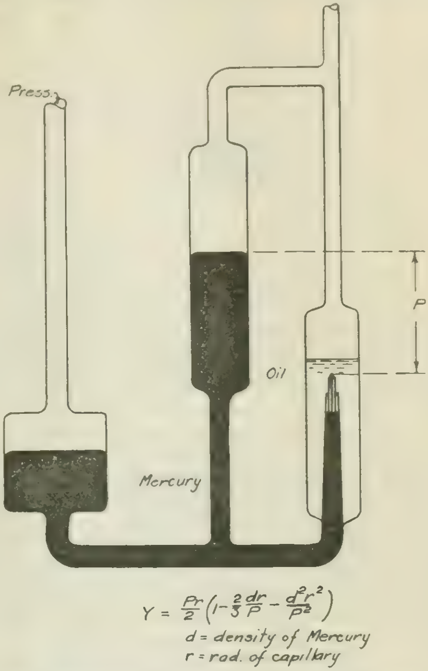


FIG. 9—APPARATUS FOR DETERMINATION OF INTERFACIAL TENSION

In order to show that not all constituents which lower the surface tension between oil and water necessarily lower the static friction coefficient, results are given on Velocite B oil containing 2 per cent of *p*-cresol. This raises, rather than lowers, the coefficient of friction, and indicates that the mere presence of an adsorbed film is not the only essential point, but that its structure is also important. This point is discussed more fully in the following section.

One difficulty with the above method of measurement with the spherical segment on a plane surface is the impossibility of determining the dry coefficient of friction, because in the absence of any liquid the segment begins to twist about on the vertical axis through its point of contact, and slowly works its way down the surface at comparatively low angles of inclination. This can be overcome by using a viscous non-lubricant, such as glycerol, which, as will be noted, gives the highest coefficients observed for these surfaces. It should be said, however, that the higher observed values for the static coefficient of friction are open to some question, since the spherical segment tends to roll slightly as the plane is raised, thus bringing new parts of the surface into contact, and this action becomes more pronounced as the angles increase. It is therefore quite possible that all the higher values tend to be crowded together by this method, preventing sharp distinctions between different kinds of mineral oil.[13]

One rather striking feature about the measurements of the static friction coefficients is that even very highly polished surfaces almost invariably produce surface scratches of quite appreciable depth when sliding actually begins, although it appears that these scratches are produced only after the slider begins to move, and therefore play no part in determining the value of the starting coefficient.

FIG. [illegible]—A[illegible] FOR DETERMINATION OF ELECTRICAL RESISTANCE OF ADSORBED OIL FILMS

SURFACE TENSION MEASUREMENTS AND THEIR SIGNIFICANCE

Probably no factor connected with the property of oiliness is so frequently mentioned without any clear notion of its true significance, as is surface tension. For example, it seems to be assumed generally that a lowering of interfacial surface tension between oil and metal must in some way *necessarily* lower the coefficient of friction, whereas there is no such necessary relationship. Even Southcombe and Wells in their extensive studies along these lines are open to serious criticism as regards their method of presentation.

When any two immiscible liquids are in contact, the molecules in the surface layers are in a partially unbalanced condition and possess a certain amount of potential energy, owing to the fact that the molecules of the one liquid do not attract those of the other as much as they attract like molecules. If this were not true the molecules of one liquid would dissolve indefinitely in the other liquid, as is the case with *miscible* liquids, and there would be no interfacial surface. Work is therefore required to bring enough molecules of each liquid from the interior of their phases to form the interfacial layers, and the amount of energy thus required per sq. cm. of interface formed is called the interfacial surface energy in ergs per sq. cm. (which is precisely equal numerically to the more frequently used, but less clearly visualized term, surface tension, in dynes per cm.).

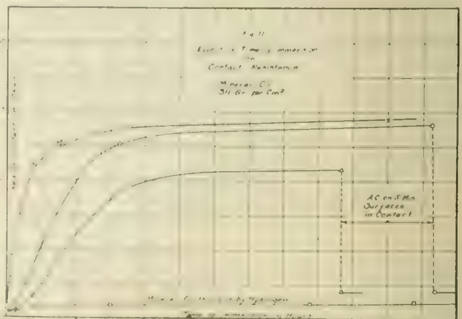
The magnitude of this interfacial surface energy, as we shall now refer to it, is readily measurable by a variety of means, the most common of which is the determination of the drop weights of one liquid when slowly dropped into another from a capillary of known diameter. In this case the force of gravity is caused to work against the forces tending to prevent the increase of surface and the drop falls when the force of gravity just exceeds the opposing forces, the magnitude of which can then be readily calculated.[14]

If molecules of some third substance are also present in one or both of the immiscible liquids, other interesting possibilities arise. Consider, for example, an interface between oil and water, with some soap present. Soap consists of a long hydrocarbon chain with an active group containing oxygen and some metal at one end. The long hydrocarbon chain is soluble in oil, but the active end with the metal atom is not. Therefore comparatively little soap will dissolve in the oil layer. On the other hand, the active end has a marked affinity for, and is quite soluble in, water, but the hydrocarbon chain prevents much of it dissolving (except in the form of a colloidal solution where the hydrocarbon chains probably form the interior of colloidal particles with the outside largely made up of the active groups).

It is obvious from these considerations that the one place where a soap molecule can be most "comfortable" is in the interface, with the hydrocarbon chain in the oil layer and the active water-soluble group in the water layer; and we would expect to find a very much higher concentration of soap at the interface than in either of the separate phases, as has actually been proved to be the case. Furthermore, the presence of this type of molecules which are, so to speak, *anxious* to concentrate in the interface, makes it easier to produce more interface. In other words, it lowers the interfacial surface energy more or less in proportion to this concentrating tendency. For substances in the molecular state the precise relation between the lowering of surface energy and the increase in concentration has been worked out on thermodynamic grounds by Willard Gibbs, but his fundamental equation does not apply quantitatively to the concentration of *colloidal* particles at the interface, though it is frequently and erroneously so used.

For the purpose in hand, therefore, a lowering of the interfacial energy is simply a measure of the tendency of certain constituents to become concentrated at an interface, and by measuring the amount of such lowering, the extent of such concentration can be roughly determined.

In an exactly similar way, there is an interfacial energy between any liquid and any solid, and the tendency of any molecules to concentrate at this interface will cause a lowering of this interfacial surface energy. Unfortunately, however, in spite of many references to this quantity as though it were definitely measurable, no method has ever been developed for measuring the interfacial surface tension between a solid and a liquid.[15] On account of this difficulty many have erroneously assumed that anything which lowered the surface tension between any two liquids would also lower



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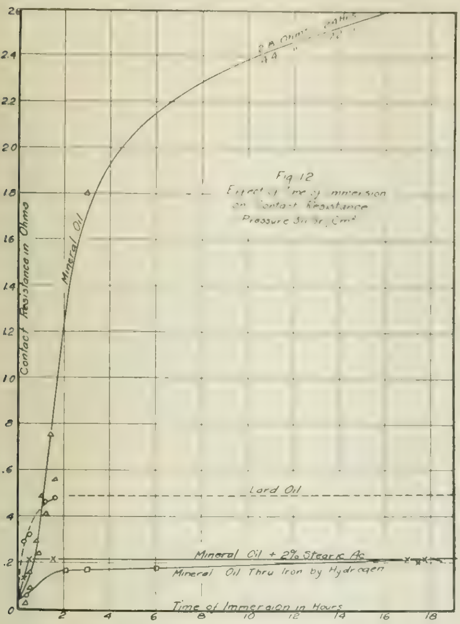
[13] [illegible] apparently been overlooked [illegible] supported on a [illegible] and polished off to a [illegible] made by Dr. Becker and Mr. H[illegible] similar to the [illegible] work has been [illegible]

[14] For a [illegible] c measurements and calculations, see Harkins [illegible]

[15] It should be said that there are some bare possibilities of arriving at an approximate measure by very special means which never yet have been carried to the limit.

the surface tension between one of those liquids and any metal. This is probably true in a very general and qualitative sense, but the two effects are by no means sufficiently parallel for the assumption to be of real value in making comparisons between different constituents of an oil, because it is obvious that the tendency of molecules to concentrate at a metal surface depends upon the attraction between these molecules and those of the metal, which would certainly be greatly different from their attraction for water molecules. In spite of this fact the writings and patent claims of Southcombe and Wells indicate their belief that anything which lowers the surface tension between an oil and *water* will decrease the coefficient of friction between partially lubricated metal surfaces.



It does seem conceivable, however, that the lowering of interfacial energy between oil and metal surfaces could be determined approximately by making measurements between oil and mercury, the only pure metal which is liquid at ordinary temperatures. At any rate the approximation would be much better than that obtainable by using water as the second liquid. This Laboratory had just completed the construction of an apparatus for such determinations when the interesting results of Bhatnagar and Garner[16] were published, and accordingly only a few preliminary measurements have thus far been made.

Bhatnagar and Garner's results with four different fatty acids dissolved in mineral oil are shown in Fig. 8. It will be noted that each has its characteristic curve, though linoleic acid seems to be more highly adsorbed than the other three. Palmitic and stearic acids give almost identical results, as would be expected from their chemical similarity.

The method developed by this Laboratory is somewhat simpler, being based on the method of Jaeger.[17] The essential portion of the apparatus is shown in Fig. 9. The interfacial tension between the mercury and the oil is measured by the head of mercury, P, necessary to cause the drops to separate from the capillary which is immersed in the oil.

The method is much more rapid, though probably not quite as accurate, as that of Bhatnagar and Garner.

Even granting, however, that the results against mercury surfaces will roughly parallel those against other metals, it must be emphasized that these results do not have any direct bearing on the coefficient of friction between partially lubricated surfaces, in spite of frequent assumption to the contrary. *Lowering of interfacial energy is only a measure of the tendency of some constituent to concentrate at the metal surface;* whether or not this results in a lowering in the friction coefficient *depends almost wholly on the nature and structure of this adsorbed film.*

This fact is brought out rather strikingly by some of the static friction measurements just discussed, in which the effect of 2 per cent additions of *p*-cresol and stearic acid to mineral oil are compared. Both lower the surface tension against mercury, both are therefore concentrated at the metal surface, but while the stearic acid film greatly lowers the coefficient, the *p*-cresol film appears to give even slightly *higher* coefficients than the plain oil.

On the basis of these and some other preliminary results, plus certain theoretical considerations, the writers believe that a partial lubricating film to be effective in reducing friction coefficients between metal surfaces under high pressures must possess the properties of a *solid* rather than of a *fluid* film, and must be of *colloidal* rather than of ordinary *molecular* dimensions. *p*-Cresol apparently fails in one or both of these specifications, while stearic acid possesses them to a high degree, as is demonstrated by some later experiments.

MEASUREMENTS OF THE ELECTRICAL RESISTANCE OF ADSORBED FILMS

As pointed out previously, interfacial energy measurements and static friction measurements show the indisputable presence of adsorbed films on metallic surfaces in contact with lubricants. They do not, however, give any definite information as to the thickness or physical characteristics of that film. The writers have therefore conducted some experiments designed to give some idea of the rate of formation and the thickness of the adsorbed film by means of its electrical resistance, with results which were far more striking than could have been anticipated. The procedure employed may be briefly outlined as follows:

A "conductivity apparatus" was constructed, as shown in Fig. 10. The oil film under examination is held between the two hardened steel surfaces, A and B. The contact faces of these surfaces (originally 1/2-in. micrometer checks) are lapped and polished true until they adhere tightly when dried and lightly pressed together. The resistance of the contact between these two surfaces was measured by means of a Wheatstone bridge so arranged that balance can be obtained either by means of a battery and galvanometer (D. C.) or microphone hummer and phones (A. C.). The tests were carried out in the following manner:

The surfaces were carefully polished and cleared, placed in the apparatus as indicated, a definite moderate pressure applied through the lever C, and the "dry" resistance was noted. This was very low, usually about 0.03 ohm when all traces of air have been removed from the surfaces by means of gentle rubbing under pressure. Part of even this was undoubtedly due to the leads and connections. The load was then removed, the surfaces separated, immersed in the oil under examination, and again placed under pressure. Some little time (about 15 min.) was required for the contact resistance to drop off to a substantially constant value.

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[16] *J. Soc. Chem. Ind.*, **39** (1920), 185T.

[17] "Temperature Coefficients of Surface Energies of Liquids," *Verslag. Akad. Wetenschappen Amsterdam*, **23** (1914), 330.

Usually the first value thus obtained was two or three times the "dry" resistance. The surfaces were again separated, immersed in the oil for a longer period of time, and then placed together and the resistance again noted. This time the observed values were very much higher. This procedure was followed at intervals for about 24 hrs., at the end of which time there was in general very little tendency toward increasing resistance. The results of a number of experiments are shown in Figs. 11 and 12. It is evident that the film increases fairly steadily in thickness for about 6 hrs., after which the curve tends to flatten off. The different curves in Fig. 11 are for the same mineral oil, Velocite B, and were obtained by regrinding and polishing the surfaces for each series of observations. The divergence indicates the lack of reproducibility, at least in these preliminary experiments. Part of the trouble is due to the difficulty of separating the surfaces after they have been in contact for some time without scraping off part of the film. This is especially true of the more tenuous portion formed after the first hour or two, which is so sensitive to rough handling that it probably plays no important part under service conditions. The first 10 or 20 per cent is much more tenaciously held, although even then vigorous rubbing or wiping will remove all but a comparatively small proportion of the total film thickness. Experiments are now being made with much higher pressures to permit distinction between lightly and firmly adsorbed films.

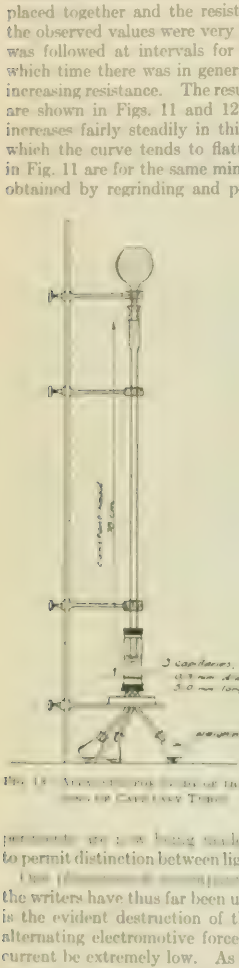


FIG. 13—APPARATUS FOR STUDY OF THE CLOGGING OF CAPILLARY TUBES

One phenomenon accompanying these experiments, which the writers have thus far been unable to explain satisfactorily, is the evident destruction of the film when subjected to an alternating electromotive force, even though the voltage and current be extremely low. As indicated in Fig. 11, after the film had attained a resistance value of 2 to 3 ohms, measured by means of the battery and galvanometer, the circuit was changed so as to impress on the film an alternating electromotive force of very low voltage, but of approximately 1000 cycles per sec. on the film, in an effort to check the measurements by means of the microphone hummer. Although the current thus passed was less than 1 per cent of the amount used in the D. C. measurements, the resistance fell off with great rapidity to the low value of about 0.4 ohm. Some more recent experiments have shown that a *heavy* direct current has precisely the same effect, presumably due in this case to heating. Since the observations do not vary appreciably regardless of the length of time the ordinary D. C. of 0.002 amperes is applied, the effects of the very small A. C. cannot be due to straight electrolysis, though they might be attributed to the action of rapidly alternating electrical stresses on a gel-like adsorbed film.

One of the most interesting features of these experiments is the surprisingly long time required for the film to build up in the case of the straight mineral oils. The most reasonable explanation of this observation appears to be that the film-forming constituents of the mineral oil are present in comparatively small proportion, and that considerable time is required for them to diffuse to the metal surface. To test this out, the same oil was shaken up for several hours with two successive portions (20 per cent by weight each) of very finely divided iron (made by reducing Fe_2O_3 with hydrogen). The iron was then separated by centrifuging and the resistance measurements repeated, with the results shown in Fig. 12. It will be noted that the resistance rises to only 8 per cent of its former value. This might, of course, be due to a decrease in the specific resistance of the film, rather than to a decrease in thickness, but careful tests did not disclose any iron soaps or suspended iron in the treated oil. It would therefore appear that a considerable proportion of the film-forming constituents had been removed by selective adsorption on the large amount of iron surface offered by the Fe by H. It is hoped also that by extraction of the adsorbed material plus the oil held in the pores and between the particles of the iron, followed by further concentration by readsorption on a smaller amount of surface, it may be possible to isolate and identify the "essence of oiliness" (?) thus separated. It will be noted that the oil thus treated showed an increase in its static coefficient of friction (see Table I).

Fig. 12 shows the results of similar experiments with lard oil and with Velocite B plus 2 per cent stearic acid, compared with the results on plain Velocite B plotted on a smaller scale.

It will be noted that the first two (which from other experiments appear to possess the greater oiliness) reach their maximum resistance much more quickly than the mineral oil, although its magnitude is much less. It is obvious, however, that the resistance cannot be taken as a direct measurement of the thickness of the film because of wide variations in the specific resistance of the different oil films, which is, for example, probably much greater for the mineral oil than for the other two. Neither is it possible to calculate the film thickness by assuming that the specific conductivity of the adsorbed film is the same as that of the oil in bulk, because the active constituents in the adsorbed film probably have conductivities of a much higher order of magnitude than the oil in bulk.

Efforts were made to arrive at a more accurate figure for the film thickness by measuring the electrical capacity of the film, since the dielectric constants of different constituents in the oil vary but little, in marked contrast to their conductivities. This was not found feasible, however, on account of the previously mentioned disrupting effect of alternating electromotive forces on the adsorbed films. Apparatus is now being constructed with which it is hoped to measure the thickness directly by means of a system of mechanical and optical levers. Meanwhile, other methods described in the next section were tried in an effort to determine how thick and adsorbed films might become under favorable conditions.

THE CLOGGING OF METAL CAPILLARIES

In view of the above-mentioned uncertainties as to the thickness of the adsorbed films, it was thought that a study of the rate of clogging of very fine metal capillaries, when an oil with film-forming tendencies was run through them, might throw some light on this subject.

Experiments were first made with capillaries approximating in dimensions those in the Standard Saybolt Viscosimeter, maintaining a small constant head at all times. These results showed that the rate of flow through glass and metal capillaries tended to decrease gradually over a period of hours, even though the temperature was accurately controlled. The change was, however, less than 5 per cent, and it was difficult to control the temperature accurately enough to distinguish sharply between different thicknesses of film.

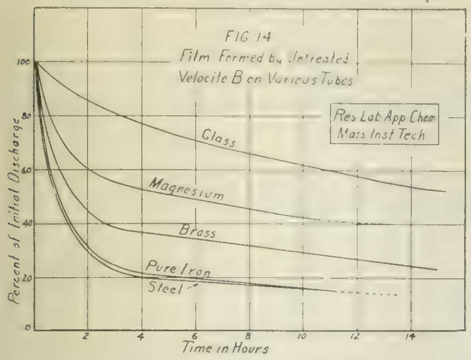


FIG 14
Film Formed by Untreated Velocite B on Various Tubes

It did confirm, however, the presence of a film of quite appreciable thickness and seemed to account for many of the difficulties which have been observed in attempting to get check measurements on lubricants of high viscosity in the ordinary viscosimeters. As a check, glass capillaries of the same dimensions were run in parallel and they showed only a negligible clogging during the period of the run.

In order to magnify the effect, recourse was therefore had to much smaller capillaries (about 0.3 mm. diameter, 5 mm. long) where the thickness of the film might become an appreciable part of the total diameter of the capillary. In order to get an accurate comparison between different types of metals and glass, three jets of almost identical dimensions were used in parallel on the same oil in all tests, the apparatus being constructed as shown in Fig. 13, on which all dimensions are given. Using such small capillaries, it was found that the results were quite erratic until the oil was filtered through 200-mesh wire gauze to remove all dust particles, etc., of a size likely to affect the results.

Most of the comparisons were made between capillaries of glass, steel, and brass of the same dimensions, through which the same oil flowed simultaneously. Observations of the rate of flow were made by weighing the efflux during 10-min. periods. The efflux during successive periods showed a marked decrease, as is indicated by Figs. 14, 15, and 16. In order to make the results comparable in spite of variations in the viscosity of the oil, and the precise size of the capillaries, all the data are plotted in terms of per cent of the weight flowing in the first 10-min. period, before appreciable clogging had time to take place, and this initial flow was always very nearly the same for all three capillaries.

Inspection of the three figures indicates, first, that the rate of clogging of the glass capillary was in all cases very much less than that of the metal capillaries, indicating a less tenacious adsorption or a thinner adsorbed film. The only cases in which the decrease even approached that of the metal capillaries was where various organic acids were added to the mineral oil. The results with the glass capillary do, however, show that the very rapid changes in flow are not due to any change in the viscosity of the oil as a whole. This is also shown by the fact that results obtained after thoroughly cleaning the capillaries always gave results which checked the original rate of flow.

Proceeding, then, to the consideration of the results with brass and steel, which more nearly measure the specific oiliness property in which we are interested, it will be noted that under the conditions of these tests, all the oils build up a film of surprising thickness, of the order of magnitude of 0.1 mm. It also indicates that the thickness of the film is greater for Velocite B than for neutral lard oil, and this fact, coupled with the static friction data, indicates that the thickness of the film, at least under comparatively low shearing stresses, is by no means the only factor of importance in determining the "oiliness" of a lubricant.

On the other hand, the effect of addition of agents such as stearic acid, oleic acid, and *p*-cresol, which other tests have shown to be adsorbed at the metal surface, is uniformly found to increase the rate of formation and thickness of the film, and in the cases of the oleic and stearic acids to stop the flow entirely after about 6 hrs.

The results on the Velocite B treated with iron-by-hydrogen confirm the previous conclusion that this treatment removes a considerable proportion of the film-forming constituents. Similar treatments with fuller's earth did not affect the thickness of the adsorbed films except possibly making a slight decrease in the case of glass.

It will also be noted that the rate of building up the film is very similar to that indicated by the resistance measurements, being rapid for a few hours and then flattening off. The film thicknesses are, however, undoubtedly much greater in the capillary experiments than in the flat disk experiments, or in lubricating practice, due to the very low rates of shear in the former case. Similar experiments are now being conducted at much higher rates of shear.

In order to prove that the clogging effect was due primarily to a selective adsorption by materials which were present in relatively small proportions, the capillaries were allowed to soak in Velocite B, although the oil was not passed through the capillaries. Upon measuring the flow after a 6-hr. soaking it was found to be 92 per cent of the normal initial flow, indicating that clogging under these conditions was inappreciable compared with the amount which took place when a large amount of oil was brought into contact with the metal surface.

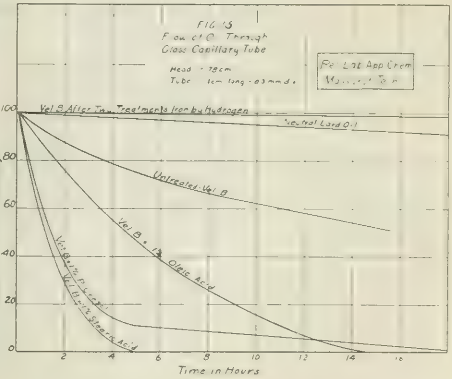
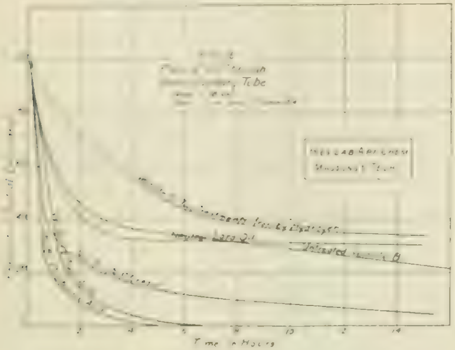
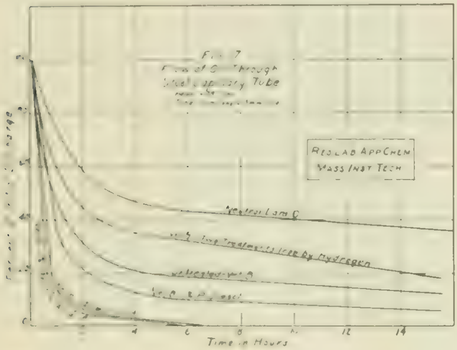


FIG 15
Flow of Oil Through Glass Capillary Tube

In order to determine whether or not this method would confirm some unpublished results of Dr. A. E. Becker, of the Standard Oil Co., which showed cast iron to be greatly superior to wrought iron or magnesium in its film-forming properties, capillaries were constructed of pure Armco iron and of metallic magnesium. The results on Velocite B with all five of the capillaries tested are shown in Fig. 17. The iron and steel check very closely, while the magnesium corresponds more nearly to glass, possibly due to the presence of an oxide film which partly saturates the normal free field of force of the metal.





From a practical standpoint, these experiments indicate the desirability of making viscosimeter capillaries from a comparatively inert material, such as glass, quartz or agate, rather than from metal, which apparently has a considerably greater tendency to clog with ordinary lubricating oils.

MISCELLANEOUS EXPERIMENTS

ADSORPTION OF STEARIC ACID BY IRON-BY-HYDROGEN—In order to throw further light on the action of the iron-by-hydrogen in removing some film-forming constituents from oil, and to demonstrate that the fatty acids were adsorbed at metal surfaces, quantitative experiments have been made on the adsorption of stearic acid from oils by very active pyrophoric iron. The iron powder was made by reducing ferric hydroxide gel with hydrogen at 450° C., the process requiring 2 wks. to give complete reduction at this temperature. The experimental procedure consisted in treating a solution of stearic acid in "Acto," a rather fluid, colorless paraffin oil, with several successive portions of pyrophoric iron, allowing the solution to stand with intermittent shaking for about 24 hrs., whizzing out the suspended iron particles, and analyzing the residual oil for stearic acid. The results of some of these experiments are given as follows:

Expt. I

Stearic acid originally present, per cent	0.60
Stearic acid left after treating [illegible] g. of solution with 10 g. of pyrophoric iron, per cent	0.28
Stearic acid removed per g. of iron, gram	0.016

Expt. II

Original concentration of stearic acid in oil, per cent	1.22
Concentration left after treating 100 g. of solution with 20 g. of pyrophoric iron, per cent	0.84
Concentration left after treatment of residual oil (90 cc.) with a second 20-g. portion of iron, per cent	0.60
Wt. stearic acid removed by first treatment (per g. of pyrophoric iron), gram	0.019
Wt. stearic acid removed by second treatment (per g. of pyrophoric iron), gram	0.011

Some experiments were also made in which incompletely reduced pyrophoric iron, or pyrophoric ferrous oxide, was used in lieu of the pyrophoric iron. The oxide appears to possess a much stronger affinity (probably chemical) for the fatty acid than the completely reduced metal, as is shown by the following results:

Expt. III

Stearic acid originally present, per cent	0.53
Stearic acid left after treating 50 g. of solution with 10 g. of pyrophoric ferrous oxide, per cent	0.04
Stearic acid removed per g. of iron oxide, gram	0.025

Although careful tests were made, in no case was there any evidence of the presence of appreciable amounts of iron stearate in the solution, although it may have been formed and immediately adsorbed.

INCREASE IN APPARENT VOLUME OF FINELY DIVIDED IRON—A few tests were made to determine whether or not the presence of the adsorbed film would increase the apparent volume of finely divided iron after centrifuging a definite weight for a definite time. The iron used in this case was very finely divided, but not pyrophoric. The apparent volume of duplicate weighed samples centrifuged from benzene checked within about 1 per cent. Other samples of equal weight shaken with oils and centrifuged 25 min. (much more than necessary to give substantially constant volume) gave the following *increases* in apparent volume:

Shaken with	Per cent Increase in Apparent Volume
Velocite B, in contact 5 hrs.	8
Velocite B, in contact 24 hrs.	14
Acto, in contact 24 hrs.	8
Acto + 2% stearic acid, in contact 24 hrs.	8+

CUTTING TESTS—A few tests were made to determine the effect of varying degrees of oiliness on the behavior of cutting lubricants. A piece of mild steel was given a deep rough cut with a "stellite" tool, taking due precautions to keep the oil as the only variable. There was a marked difference in the smoothness of the resulting cuts, the lard oil being the smoothest, Velocite B plus 1 per cent stearic acid a close second, plain Velocite B much rougher, and Velocite B heated with sulfur worst of all. Even more striking results have recently been obtained by Bingham and others at the Bureau of Standards.

While these tests were a satisfactory confirmation of the previous conclusions as to oiliness, there seemed to be no way to make the comparisons quantitative, and further work was accordingly discontinued.

METHODS APPROXIMATING SERVICE CONDITIONS—There are three very promising methods of investigating the effect of oiliness in a manner approaching service conditions, two of which were mentioned in the previous paper. They are:

1—Investigation of the effect of oiliness on the critical value of zn/p in a normal full bearing. This Laboratory is now undertaking such tests using a Sperry gyro-compass and applying high loads by processing the gyro.

2—Investigation of the length of time bearings will continue to operate with a moderate coefficient of friction after the oil feed has been discontinued. Viscosity is also a variable affecting these results, but can be practically eliminated in a series of comparative tests between oils of similar viscosity but varying composition.

3—Investigation of the power losses in gears under heavy loads and lubricated by oils.[18] Some interesting results have been obtained by this method in England,[19] which confirm the superiority of vegetable and animal over mineral oils under these conditions of partial lubrication.

ACKNOWLEDGMENT

The writers desire to acknowledge the courtesy of the General Motors Research Corporation and of the Standard Oil Company of New Jersey in permitting the publication of these results; and the invaluable assistance of Messrs. Harry Myers and Tyler Fuwa of this Laboratory, who have made all the static friction measurements and capillary clogging measurements, respectively.

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[18] Tests with greases are not satisfactory from this standpoint because so much of the friction is in the mass of grease itself, rather than between the gear teeth.

[19] Report of Lubricants and Lubrication Committee, Department of Scientific and Industrial Research, Advisory Council, 1920.

Comparison of the Standard Gas Furnace and Micropyrometer Methods for Determining the Fusibility of Coal Ash[1,2]

By A. C. Fieldner,[3] W. A. Selvig and W. L. Parker

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Coal ashes showing a softening temperature under 2600° F. by the gas furnace method can in the majority of cases be checked within 100° F. by the micropyrometer method if fused in a reducing atmosphere of combustion gases similar to that employed in the gas furnace method. Some coal ashes will, however, show considerably greater differences between the two methods.

Very refractory ashes, showing a softening temperature above 2800° F. as determined by the gas furnace method, tend to give considerably lower results by the micropyrometer method. The great majority of ashes from American coals, however, fuse below 2800° F. in the gas furnace.

The two methods can therefore not be considered as strictly alternate methods for all ashes. In general, the micropyrometer method shows a point in the fusion process at which the particles become rounded and coalesce. This point agrees fairly well with the "down point" of the cones in the gas furnace method for ashes of low and medium fusibility (up to 2600° F.), since such ashes form a fairly fusible slag of short softening range. Refractory ashes form viscous slags with long softening intervals; therefore the down point of the cone may be from 100° to 500° F. higher than the fusing point as shown on the platinum strip.

The micropyrometer method with reducing atmosphere has the advantage over the gas furnace in being much more rapid (fifty determinations can be made in a day of 8 hrs. as compared to fifteen on the gas furnace) and in dispensing with the special ashing of a quantity of coal. The residue of the usual ash determination is sufficient for tests; also it is more comfortable to the operator.

Some checks between different laboratories indicate that the micropyrometer method can probably check itself in the hands of different operators as closely as the gas furnace method. Further work should be done on this phase of the subject.

It may be advisable to adopt both methods as tentative, although not alternate until such a time as experience will show which is preferable.

COAL ash is a mixture of substances and therefore does not have a definite melting point. The fusion or softening temperature depends on a number of variables and consequently must be empirically defined in order that reproducible results may be obtained in different laboratories. At the present time the American Society for Testing Materials[4] has tentatively defined the softening temperature of coal ash as the temperature at which a triangular pyramid 0.75 in. high and 0.25 in. at each side of base, mounted vertically, has fused down to a spherical lump when heated in the reducing atmosphere of a gas furnace under definitely prescribed conditions.

Recently Mr. W. H. Fulweiler, Chemical Engineer of the United Gas Improvement Company, applied to coal ash the micropyrometer method[5] of determining the melting points of minute specimens. The advantages claimed for the micropyrometer over the gas furnace method are greater speed, convenience, and comfort to the operator in making fusion tests. In order to obtain data on the comparative results by the two methods, fusion tests were made on a series of coal ashes of varying fusibility, ranging from 1800° to 3000° F. by the gas furnace method.

MICROPYROMETER APPARATUS

The micropyrometer apparatus as used in making the tests was assembled from apparatus available in the laboratory. A diagrammatic sketch showing the arrangement of the equipment for making fusion tests in air is given in Fig. 1.

The heating element consists of a platinum strip 4 cm. long × 0.5 cm. wide × 0.008 cm. thick held between the iron rods *h* which are connected through the spiral nichrome resistance coil *t* to four storage battery cells, *a*, connected in series. The maximum current required to attain temperatures as high as 2850° F. is 45 amp. From 10 to 15 amp. of the total current are supplied from a direct current power line which is connected through the adjustable rheostat *d* in parallel with the storage batteries. Rheostat *d* also serves as a charging rheostat in charging the storage batteries, *a*.

The platinum resistance strip *i* is enclosed in a small alundum furnace, *j*, which is divided into two parts, the upper half of the furnace being removable and provided with an observation hole over which is placed a microscope cover glass. The furnace rests on the stage of the microscope *k*. The microscope is provided with a 48-mm. objective and a 6x ocular. The ocular contains a small, tungsten, hairpin

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[1] Received March 20, 1922. Presented before the Division of Industrial and Engineering Chemistry at the 63rd Meeting of the American Chemical Society, Birmingham, Ala., April 3 to 7, 1922.

[2] Published by permission of the Director, U. S. Bureau of Mines.

[3] Superintendent, Pittsburgh Experiment Station.

[4] "Tentative Method for Determination of Fusibility of Coal Ash," *Proc. Am. Soc. Test. Materials*, **20** (1920), 796.

[5] G. K. Burgess, "A Micropyrometer," *Bur. Stds., Bull.* **9**, No. 4 (1913), 475.

filament lamp so adjusted that the filament coincides with the image plane of the eyepiece. A piece of monochromatic red glass mounted in a removable cap is slipped over the top of the eyepiece. A removable cap containing a pinhole in its center is placed over the monochromatic glass on top of the eyepiece. The terminals of the lamp are connected through slide-wire resistances, *p* and *q*, through the switch *r* to a milliammeter, *s*. Current for the lamp is supplied from two dry cells, *o*. A fixed resistance, *m*, consisting of resistance wire mounted in an Economy fuse plug is connected in parallel with the pyrometer lamp. This resistance is so adjusted as to give the maximum deflection on the milliammeter for the temperature range for which the pyrometer lamp is calibrated.

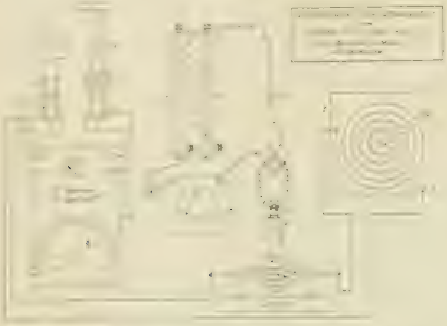

FIG. 1—MICROPYROMETER APPARATUS FOR DETERMINATION OF FUSIBILITY OF COAL ASH

a, 4 chloride cell storage batteries (Type [illegible]) Electric Storage Battery Co.
b, Fuse—[illegible] amp.
c, Knife switch to furnace "J" (80 amp.)
d, Cutler Hammer charging rheostat (max. capacity, 20 amp.)
e, Knife switch
f, Fuses—25 amp.
g, Knife switch—60 amp.
h, [illegible] rods for holding platinum strip
i, Platinum strip 4 cm × [illegible] cm × 0.003 in. thick
j, Alundum furnace
k, Microscope, [illegible] x ocular, 48 mm. objective
l, Tungsten hairpin filament lamp, 2.6 volt, 0.4 ampere (Edison Mine Safety Lamp bulb, B. M. 10)
m, Fixed resistance in parallel with pyrometer lamp (28 gage "Tarnac" wire in Economy fuse plug)
o, Two dry cells in series
p, Slide wire resistance coil (1 ohm)
q, Slide wire resistance coil (2.8 ohms)
r, Knife switch
s, Milliammeter (scale, 0 to 750 milliamperes)
t, Spiral nichrome ribbon resistance coil (ribbon 1¼ in. wide, 29 B. and S. gage)

METAL FURNACE FOR REDUCING ATMOSPHERE

For obtaining a reducing atmosphere surrounding the ash an airtight cylindrical brass furnace shown in Fig. 2 was made. The inlet tube of the brass furnace was connected by means of rubber tubing through a bottle to catch condensed water, to a porcelain tube which was inserted in a small Méker muffle furnace. The muffle furnace was modified by removing the muffle and replacing it with a porous alundum tube about 1.25-in. internal diameter. The open front of the furnace around the alundum tube was closed with alundum cement. A small disk of alundum cement was inserted into the projecting end of the alundum tube and the porcelain tube inserted through a small hole in the center of the disk into the furnace. The furnace was heated by means of a Méker blast burner to a temperature of about 900° C. To insure an excess of reducing gases the furnace was operated so as to have a flame of about 3 to 5 in. issuing from the top of the chimney. The gas from the muffle furnace was aspirated through the metal pyrometer furnace by connecting it to a [illegible] water pump through a Mariotte flask and a flask containing water through which the gas was bubbled to indicate the rate of flow. Samples of gas as delivered into the metal pyrometer furnace were taken at various times when the Méker furnace was operated under the conditions described, and the analyses of the gas samples showed that its composition remained very uniform. As considerable water condensed in the tubes connecting the metal pyrometer furnace to the Méker gas furnace, the water content of the gas delivered into the pyrometer furnace was calculated by assuming the gas to be saturated with water vapor at the temperature at which it was collected. The analyses of the gas samples are given in Table I.

TABLE I—COMPOSITION OF FURNACE ATMOSPHERE USED IN MAKING MICROPYROMETER FUSIBILITY TESTS IN REDUCING ATMOSPHERE OF COMBUSTION GASES

	PERCENTAGE BY VOLUME						
SAMPLE NO.	CO_2	O_2	H_2O	H_2	CO	CH_4	N_2
1	5.7	0.5	2.7	7.5	8.7	0.9	74.0
2	5.6	0.2	2.7	8.1	8.8	0.6	74.0
3	6.6	0.4	2.7	7.6	7.0	0.0	75.7
4	5.2	0.3	2.7	8.5	9.3	0.9	73.1
5	6.2	0.4	2.7	7.4	7.4	0.0	75.9
Av.	5.9	0.4	2.7	7.8	8.2	0.5	74.5

Total oxidizing gases ($CO_2 + O_2 + H_2O$) = 9.0 per cent
Total reducing gases ($H_2 + CO + CH_4$) = 16.5 per cent
Ratio of reducing gases to oxidizing gases = 65 : 35

Experimental work done by the Bureau[6] with hydrogen and water vapor mixtures, and carbon monoxide and carbon dioxide mixtures indicate that the gas mixture need only be controlled between 30 and 70 per cent reducing gas to insure the lowest softening temperature of coal ash. The ratio of reducing gases to oxidizing gases (65:35), as shown in the average analysis of the gas used in the brass micropyrometer furnace, comes within these limits.

CALIBRATION OF PYROMETER LAMP

The pyrometer lamp was calibrated and checked at frequent intervals by melting small portions of pure gold, diopside, and palladium on the platinum strip of the micropyrometer furnace. The lamp filament was matched against a clean spot on the platinum adjoining the fused material.

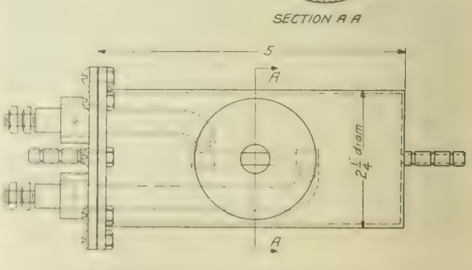

FIG. 2—FURNACE FOR REDUCING ATMOSPHERE

FIG. 2—METAL FURNACE AND REDUCING ATMOSPHERE

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[6] A. C. Fieldner, A. E. Hall and A. L. Feild, "The Fusibility of Coal Ash and the Determination of the Softening Temperature," *Bur. Mines, Bull.* **129** (1918), 49, 53.

The same procedure was followed in determining the fusion point of the coal ash. A calibration curve was drawn through the three points obtained with gold, diopside, and palladium, the temperatures required to melt these substances being taken as 1063°, 1391°, and 1549° C., respectively.

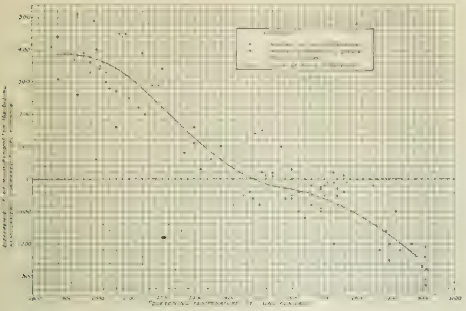

Fig. 3—Graphic Representation of Variations of Fusibility of Coal Ash as Determined by Micropyrometer Method in Air and Gas Furnace Method

Method of Making Fusibility Tests in Oxidizing Atmosphere of Air

The coal ash remaining from the determination of ash in the proximate analysis of the coal was ground to an impalpable powder in an agate mortar. A portion of the finely ground ash was moistened with distilled water and a small amount transferred by means of a glass rod drawn to a point to a piece of platinum foil about 3 mm. square. One corner of the platinum foil was turned up so it could be readily picked up with a pair of forceps. The platinum foil with the ash was placed on the platinum heating strip and adjusted so as to be in the center of the field of the microscope. The upper part of the furnace was put in place and the observation hole covered with a microscope cover glass. The temperature was raised by means of the resistance *t* until the ash showed distinct fusion under the microscope. The temperature reading was taken by adjusting the current through the pyrometer lamp by means of the slide wire resistances *p* and *q* until the tip of the lamp filament disappeared when focused against a clean spot on the platinum foil near the fused coal ash. The temperature of the platinum heating strip could be raised by proper manipulation of rheostat *t* with one hand, and at the same time the current going through the pyrometer lamp could be adjusted by manipulating the slide wire resistances *p* and *q* with the other hand.

The point taken as the fusion point of the ash was that at which the irregular-shaped aggregates of ash particles showed a well-defined rounding under the microscope. Care should be taken that the fusion point is not confused with a sintering of the ash, and in case of doubt it should be examined after the determination at a higher magnification than that used in making the determinations.

Method of Making Fusibility Tests in Reducing Atmosphere of Combustion Gases

After the ash sample had been placed on the platinum heating strip of the brass micropyrometer furnace, the combustion gases generated in the Méker furnace were rapidly aspirated through the brass furnace for 5 min., after which the gas flow was regulated to 3 to 4 bubbles per sec. and the fusibility determination made in the manner described.

Comparison of Micropyrometer and Gas Furnace Results

In order to compare the results obtained with the micropyrometer in both oxidizing and reducing atmospheres with the fusibility as determined by the gas furnace method, representative coal ashes covering a wide range of fusibility were selected.

The tentative method for the determination of fusibility of coal ash adopted by the American Society for Testing Materials[4] consists of heating finely ground coal ash, molded into triangular cones, 0.75 in. high and 0.25 in. at each side of the base, at a rate of heat increase of not less than 5° or more than 10° C. per min. in a pot furnace, with proper regulation of air and gas so as to obtain an atmosphere sufficiently reducing to reduce the ferric oxide in the coal ash principally to ferrous oxide, which conditions give the lowest temperature at which fusion occurs. The point taken as the fusion point is designated as the "softening temperature," and is defined as the temperature at which the cone has fused down to a spherical lump.

For convenience the coal ashes selected were subdivided into three groups according to the "softening temperatures" obtained with the gas furnace method:

Easily fusible ashes, softening below 2200° F.
Ashes of medium fusibility, softening between 2200° and 2600° F.
Refractory ashes, softening above 2600° F.

The coal ashes were run by the gas furnace method and by the micropyrometer method in an oxidizing atmosphere of air and in a reducing atmosphere of combustion gases. The variations of the micropyrometer determinations in an oxidizing atmosphere of air from the gas furnace determination are given in Fig. 3. The variations of the micropyrometer determinations in a reducing atmosphere of combustion gases from the gas furnace determinations are given in Fig. 4. In a few instances, with the very refractory ashes, sufficiently high temperatures were not attained in the gas furnace to reach the "softening temperature" of the ash samples, although these ashes were fused by the micropyrometer method. Such ashes are indicated in the figures by a cross sign (×), and the differences between the methods is greater than that indicated.

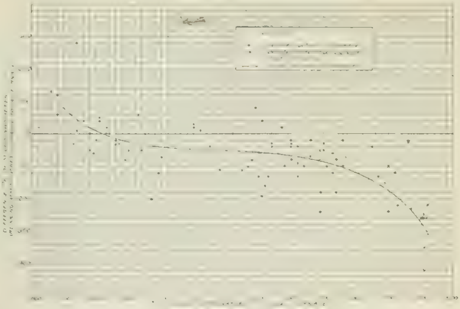

Fig. 4—Graphic Representation of Variations of Fusibility of Coal Ash as Determined by Micropyrometer Method in Reducing Atmosphere of Combustion Gases and Gas Furnace Method

It will be noted that with easily fusible coal ashes, softening under 2200° F., the micropyrometer method with an oxidizing atmosphere of air gives much higher results than the gas furnace method, but that when the same ashes are run by the micropyrometer method in a reducing atmosphere of combustion gases much closer checks are obtained between the gas furnace and micropyrometer. With ashes of medium fusibility and refractory ashes there is no marked difference between the results obtained with the micropyrometer method in oxidizing or reducing atmospheres.

The consistently high results obtained on easily fusible ashes when fused by the micropyrometer method in air are unquestionably due to the high iron content of such ashes, which necessitates careful consideration of the atmosphere in which the ashes are fused. An oxidizing atmosphere will oxidize the iron to the ferric state, which gives more refractory silicates than are obtained when the iron is reduced principally to the ferrous state, a condition which results in the reducing atmosphere of the gas furnace method. Fig. 4 shows that much closer checks on the easily fusible ashes are obtained between the micropyrometer and gas furnace when an atmosphere similar to that obtained in the gas furnace is used.

It will be noted that with the very refractory ashes the micropyrometer method tends to give lower results than the gas furnace. This difference appears to be the greatest in ashes fusing above 2800° F. in the gas furnace. A number of such ashes were made into cones and heated in the gas furnace just up to the temperature where fusion was evident by the micropyrometer method, after which the cones were examined under a microscope. Although sufficient fusion had not resulted to cause the cones to assume a spherical shape, the ash of the cones had a fused appearance when examined under the microscope. In some cases the cones still retained their original shape. Owing to its complex composition coal ash has no definite, sharply defined melting point. When subjected to heat there is a distinct temperature interval in the gas furnace method between the time when the ash cone first shows an indication of fusion as evidenced by the rounding or bending of the tip and the time when the material has become sufficiently fluid to flow down to a spherical lump.

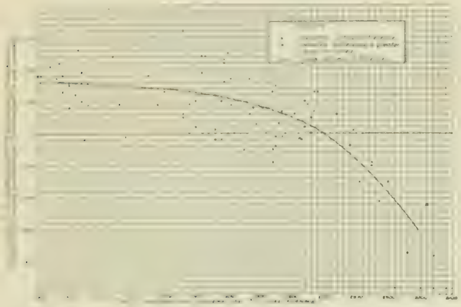

FIG. 5—GRAPHIC REPRESENTATION OF VARIATIONS OF FUSIBILITY OF COAL ASH AS DETERMINED BY MICROPYROMETER METHOD IN REDUCING ATMOSPHERE OF COMBUSTION GASES AND "INITIAL DEFORMATION TEMPERATURE" OF GAS FURNACE METHOD

With highly refractory ashes there is sufficient fusion of eutectic mixtures to give a distinctly fused appearance under the microscope, but at such temperature with the [illegible] method sufficient unfused material is present to prevent any great deformation of the cone. However, the large majority of coal ashes fuse by the gas furnace method below 2800° F., and the extreme variations shown in Figs. 3 and 4 represent exceptionally refractory coal ashes.

Fig. 5 gives the correlation between the temperature when fusion occurred with the micropyrometer method in a reducing atmosphere of combustion gases and the "initial deformation temperature" of the gas furnace method, the temperature at which the first indication of fusion is observed as indicated by the rounding or bending of the apex of the ash cones. With the majority of coal ashes the micropyrometer fusion point is higher than the "initial deformation temperature" of the gas furnace, although it will be noted that very refractory coal ashes will show distinct fusion under the microscope at temperatures lower than the "initial deformation temperature" of the gas furnace.

RESULTS OF CHECK DETERMINATIONS BY DIFFERENT LABORATORIES

Five samples of coal ash covering a wide range of fusibility, from 2000° to 3000° F., as determined by the gas furnace method, were sent to eight laboratories for fusibility determinations. Five laboratories determined the ash fusibility by the gas furnace method of the American Society for Testing Materials, and three laboratories determined ash fusibility by the micropyrometer method in an oxidizing atmosphere of air. The laboratories were asked to submit the first three results obtained on each ash and not to run duplicate determinations at the same time. The individual laboratories checked themselves closely on each ash, and in this respect there is no apparent difference between the two methods, as individual operators can check within 50° F. on duplicate determinations. The average values reported by the different laboratories are given in Table II. Further checks between different laboratories should be made with the micropyrometer method in a reducing atmosphere of combustion gases comparable to that of the gas furnace.

TABLE II—AVERAGE OF THREE FUSIBILITY TESTS BY DIFFERENT LABORATORIES ON FIVE STANDARD COAL ASHES BY GAS FURNACE METHOD AND MICROPYROMETER METHOD IN OXIDIZING ATMOSPHERE OF AIR

LABORATORY	Ash 1 ° F.	Ash 2 ° F.	Ash 3 ° F.	Ash 4 ° F.	Ash 5 ° F.
	GAS FURNACE METHOD				
A	2060	2320	2500	2730	+2900
B	2050	2350	2480	+2660	+2640
C	2000	2270	2420	2610	2800
D	2060	2380	2550	2740	3000
E	2000	2220	2370	2580	....
Av.	2030	2310	2460	+2660	+2840
	MICROPYROMETER METHOD, IN AIR				
A	2180	2280	2340	2500	2620
F	2260	2330	2360	2610	2750
G	2250	2350	2440	2550	2600
Av.	2230	2320	2380	2550	2660

News from Canada

That the foundation of scientific control lies in good will and intelligent coöperation is the view of leading men in Canada's pulp and paper industry. This was strongly evidenced at the summer meeting of the Technical Section of the Canadian Pulp and Paper Association, held at Iroquois Falls, Ontario, June 19 to 22, as guests of the Abitibi Power and Paper Company.

The Abitibi Company employs 1125 men, makes more newsprint a day than any other mill, and operates the largest machines in the world. Twenty feet is quite a width to make a sheet of newspaper and to keep flat so that it will run smoothly on the big fast presses, but the Abitibi people are running two of this size at the rate of 650 ft. a minute, and their output would cover a six-acre field in 10 min.

One of the most important parts of this plant is the Service Department, which includes the science part of the business. At the time of our visit the laboratories were working on cymene, sulfur, and uniformity of product. This department is also the educational agent, and maintains a well-equipped classroom where night school is carried on and production records are shown by means of lantern slides.

Bids for the construction of the chemical building of Loyola College, Baltimore, Md., have been received, and announcement of the awarding of the contract is expected in the near future.

Nitrogen Fixation by the Cyanide Process[1,2]

By F. E. Bartell

University of Michigan, Ann Arbor, Michigan

An earlier paper has described the production of ammonia by the sodium cyanide method. The present paper deals with the study of the cyanizing end of the ammonia process.

The results given in this paper were obtained with 4-in. batch retorts with a capacity of 8 lbs. of briquets and with technical sized 8-in. continuous retorts, with a maximum cyanizing capacity of not less than 50 lbs. of cyanized briquets per hr.

In studying the progress of the cyanizing reaction in the 4-in. retorts, the retort was arbitrarily divided into five zones, heated to approximately the same temperature, and the extent of reaction in the zones was compared. The amount of cyanide formed in each zone was largely dependent on the concentration of carbon monoxide gas in that zone, a high concentration of the gas holding down cyanide formation.

Some of the carbon used in cyanide formation came from decomposition of carbon monoxide. Iron used in the original mixture was oxidized to Fe_2O_3 and Fe_3O_4, during the process of making and drying the briquets. The reduction of this oxide during the cyanizing process was slight in the upper heat zones, even though it was in the presence of carbon and carbon monoxide at 1000° C. The repression, which is much as would be expected from a system higher in carbon dioxide content, is being studied further.

The paper also records large-scale work, in which 3- to 12-day runs were made. The work was done in 8-hr. shifts and yields were based on the performance of each shift. A normal production of 7 to 8 lbs. of sodium cyanide per retort per hr. was obtained, and this was finally increased to as high as 12.19 lbs. per retort per hr.

Conservative cost estimates showed that ammonia could be produced by this method for approximately 30 cents per lb., which represented a cost of cyanide production in briquets of approximately 10 cents per lb.

Just before the Armistice, the method for the fixation of nitrogen as cyanide and the subsequent conversion of cyanide into ammonia and nitrates had been developed to a point where positive results were assured. At that time preliminary plans were actively under way by the War Department for the construction of a plant for the fixation of nitrogen by this process.

Late in 1917 the author of this paper was assigned by the Nitrate Division of the Ordnance Department to study the Bucher process for the fixation of nitrogen, and to attempt the development of a process by which cyanide formed thereby could be converted into ammonia and ammonium nitrate. The latter part of this work has already been described in a previous paper.[3] In that paper it was shown that the conversion of cyanide to ammonia could be satisfactorily accomplished. It was known, however, that the cost of cyanide production with the process as developed at that time would be high; consequently a research was organized to study the cyanizing end of the ammonia process.[4] This work was to be carried on simultaneously with the ammonia research.

Experimental work on the cyanizing of briquets was begun in the laboratories of the Nitrogen Products Company at Greene, R. I., early in April 1918, and was continued until the middle of November of that year.

In general, the plan of the investigation was along the following lines:

1—A study of different types of coke and a comparison of their reactivity and suitability for the production of cyanide.

2—A study of the effect of different compositions of briquet material.

3—Rate of reaction and chemical equilibria involved.

4—Progress of reaction in technical sized units.

5—Application of above findings to commercial operation.

A method for the preparation of sodium cyanide by the Bucher process was described in detail in This Journal in 1917.[5] According to the author of that paper, the process was one which should offer practically no difficulties either chemically or mechanically, even when carried out on a large scale. It was pointed out, also, that the process "makes use of the crudest things such as coke, producer gas"—soda ash and also some iron which is supposed to function as a catalyst. It was further stated that we "can use producer gas just as well as nitrogen" and that the process could best be carried on at a temperature of from 900° to 950° C. The reaction is shown by the following equation:

$$Na_2CO_3 + N_2 = 2NaCN + 3CO - 138500 \text{ cal.}$$

It was discovered early in our work that the process offered no serious difficulties chemically, but that much room remained for improvements mechanically. It was seen that owing to the reversibility of the various reactions, close correlation between the progress of the chemical reactions and mechanical treatment was necessary in order to obtain high yields.

When properly treated the precise nature of the coke used made little difference in the maximum yield of sodium cyanide.

The exact proportions of the carbon, soda ash, and iron in briquets was of far less importance than was the exact manner of bringing these constituents together and of their later treatment. The existing chemical equilibria, especially the equilibria dependent upon the concentration of the components of the gaseous phase, was of the greatest importance.

In a continuous process, the length of time of heating was highly important. Large retorts, externally heated, offered a serious problem, owing to the low thermal conductivity of the reactive mass coupled with the fact that the reaction is endothermic.

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[1] Received February 28, 1922.

[2] This article is printed with the approval of the Chief of Ordnance, U. S. A., also with the approval of Mr. Edward E. Arnold, President of the Nitrogen Products Company. The author wishes to acknowledge the able assistance rendered by his associates in this work, all of whom should share equally with him any credit which may arise from it.

The men in charge of the more important phases of this work were: Mr. Donald V. Lowe (formerly Lieut., Ord. Dept., U. S. A.), Mr. H. E. Kaiser, Mr. O. E. Madison, Mr. Paul A. Keene, Mr. E. J. Bird, Mr. G. H. Loselle, and Mr. L. A. S. Rapin (chemists and chemical engineers).

[3] This Journal, **14** (1922), 516.

[4] During 1918, a 10-ton per day plant was built under the direction of the Bureau of Mines for the War Department. This plant was completed just about the time of the Armistice, so that little had been done along the line of obtaining data during actual operation of the process. Brown, This Journal, **11** (1919), 1010.

[5] Bucher, This Journal, **9** (1917), 233.

OUTLINE OF WORK

Three lines of work were carried on simultaneously:

1—In the chemical laboratory experiments were conducted in a 1-in. iron retort about 3 ft. in length, with a heat zone of about 2 ft. This retort was heated in a small Fletcher gas furnace.

VIEWS OF THE EXPERIMENTAL CYANIZING PLANT, GREENE, R. I.

2—Small scale work was carried on with 4-in. iron retorts 4.5 ft. in length with a heat zone of approximately 3 ft. The capacity of these retorts was approximately 8 lbs. of briquets. Experiments with these retorts were carried on in a manner closely conforming to actual operation of a technical sized unit.

3—Two technical sized units, quite similar to those in the Saltville plant, were installed, and all significant findings from the small scale work were applied in runs with these larger units.

The main object of the present paper is to outline the results obtained in the actual operation of a technical unit; accordingly, only results obtained in work under divisions 2 and 3 will be given. A more exact study of the complete chemical equilibria of the process (part 1) was not quite completed at the time of the conclusion of the work at Greene. The author has since continued this work. A separate paper covering this phase will follow later.

SMALL SCALE WORK WITH 4-IN. BATCH RETORTS

In this small scale work, 4-in. retorts 4.5 ft. in length were used. These retorts were supported vertically in the furnace and were heated to a temperature of approximately 1050° C. by means of oil burners. By a proper arrangement of baffles at the bottom of the furnace the hot gases were deflected in such a way as to result in a fairly uniform distribution of heat throughout the furnace.

In order to study intelligently the progress of a cyanizing reaction, it was first necessary to know to what extent it was possible to obtain duplicate results in different experiments. A series of experiments was planned in which operations were practically identical in each case.

The first fifteen experiments with the 4-in. retorts gave a variability of sodium cyanide formed in the briquets ranging from 10.1 to 32.7 per cent. The average for the fifteen experiments was 16.7 per cent. This represents about the limit of variability in practice when the system is not under rigid control. After many runs, during which all factors, such as temperature control, rate of gas flow, method of placing material in retorts, uniformity of briquets, method of sampling, etc., were brought under control, results could be more closely duplicated. As an example, a series of five successive runs gave 29.40, 31.05, 29.05, 32.15, 28.60 per cent. Average = 29.93 per cent. (This represented an average conversion of approximately 82 per cent of the sodium carbonate originally present.) These figures represent just about the limits of variability of the results obtained in the small scale work described in this paper. Also this variability represents just about the limits obtained in our best large scale work.

The composition of the briquets used in practically all the experimental work described below was approximately: 50 per cent C, 38 per cent Na_2CO_3, and 12 per cent Fe, which upon oxidation of the iron became 48 per cent C, 36.5 per cent Na_2CO_3, and 16.5 per cent Fe_3O_4.

A petroleum coke of the following composition was used in making the briquets: Carbon = 96.95 per cent; moisture = 0.56 per cent; volatile matter = 1.01 per cent; ash = 1.48 per cent.

The length of the entire heat zone of the retort was 35 in. After each run the briquets were carefully removed from the retort so as to give as nearly as possible five equal portions from this heat zone (7 in. each), as indicated in Fig. 1. An analysis was made on a uniform sample from each portion.

In carrying out the experiments the same volume of briquets was used in each run; the briquets were added until they extended from the lower limit of Zone 5 to the upper limit of Zone 1. By adopting this method a slight difference in weight at times resulted—due to the slight differences in physical properties of the briquets and the manner of packing in the retort. The average weight of briquets introduced was approximately 7 lbs. The variation from this weight was probably in no case greater than about 2 per cent.

In carrying out a run the briquets were placed in the retort, the burners turned on, and the furnace gradually brought to a temperature of approximately 1060° C. within a 30-min. period. An attempt was made to hold the temperature of the retort at 1050° C., but owing to passage of nitrogen gas through the retort and to heat radiation from the furnace, there was a temperature gradation within the retort of from approximately 1050° C. in Zone 4 to approximately 1020° C. in Zone 1. As soon as the furnaces reached the desired temperature the time was taken as the beginning of a run. A definite though small volume of nitrogen, which was passed through a pyrogallate solution to remove oxygen, was forced upward through the retort from the beginning of the heating. At the beginning of a run, a definite, larger volume was passed.

PROGRESS OF REACTION

In this study 160 individual runs were made. These runs were planned so as to cover time intervals of 0.5 hr., 1 hr., 1.5 hrs., and 2 hrs. For the discussion of results there are chosen for comparison averages of three successive runs made near the end of this series after all the variable factors were fairly well under control. These runs all appeared to be typical for the time interval in question.

The average composition of briquets used in these different runs varied only slightly. The exact composition at the beginning and at a given stage in the reaction is shown in Tables I and II.

TABLE I—COMPOSITION OF BRIQUETS BEFORE AND AFTER TREATMENT

Per cent of	Before Cyanizing	Composition of Briquets After 1 Hr. Zone 1	2	3	4	5	Composite Composition of Each Material in Retort
Fe	0.11	0.18	0.26	0.37	3.12	9.09	2.98
Fe_3O_4	15.34	9.03	11.74	14.07	13.14	10.85	12.6
Na_2CO_3	37.43	42.05	38.70	32.22	22.08	12.40	28.6
C	47.12	46.00	46.3	49.7	55.00	53.00	49.2
NaCN	0.00	1.82	2.94	3.63	6.55	14.24	6.65

TABLE II—COMPOSITION OF ZONE MATERIAL BY WEIGHT (IN OZ.) AFTER CYANIZING

Zone No.	Zone Weight[1]	Fe	Fe_3O_4	Na_2CO_3	C	NaCN
1	16.5	0.05	2.37	6.95	6.66	0.47
2	25.3	0.07	2.92	9.5	12.06	0.75
3	17.5	0.06	2.46	5.64	8.71	0.63
4	16.3	0.52	2.15	3.71	8.75	1.17
5	25.7	2.31	2.89	3.2	13.61	3.69
Total weight in retort after cyanizing	101.3	3.01	12.7	29.00	49.79	6.71
Weight before cyanizing	110.0	0.12	16.9	41.2	51.8	0.00
Change in weight	+8.7	+2.89	−4.11	−12.2	−2.01	+6.71

[1] The rather large differences in zone weights are due, in this set of runs, to inaccuracies in apportioning zone volumes as the materials were removed from the retort.

In this series of experiments heating was stopped at the end of the 1-hr. period. Nitrogen gas was passed through the retort very slowly until the briquets were cool, after which the contents of the different heat zones were analyzed.

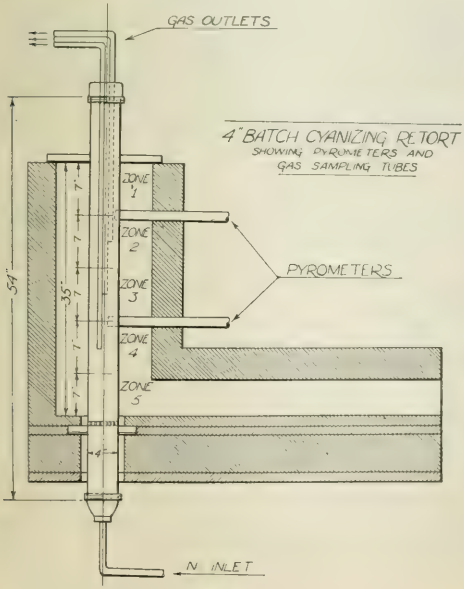

FIG. 1

Analysis was made for sodium cyanide, sodium cyanate, sodium ferrocyanide, sodium carbonate, free iron, and iron oxide. Carbon was determined by difference.

REACTIONS—The principal chemical changes in this process are due to the following reactions:[6]

$$Na_2CO_3 + 4C + N_2 = 2NaCN + 3CO \quad (1)$$

weight changes 106 + 48 = 98 (+ 56 loss from retort)

$$Fe_3O_4 + 4C = 3\,Fe + 4CO \quad (2)$$

weight changes 232 + 48 = 168 (+ 112 loss from retort)

In order to follow the changes which occurred within the retort during the reaction we will take the average of three typical runs in which a complete analysis of material present was made after a 1-hr. heating period.

During a number of the runs, similar in all respects to those above described, three small ($^1/_8$-in.) iron tubes were inserted down through the center of the retort in such a manner that samples of gas could be removed slowly from the reaction zones at different intervals during an experiment. The tubes extended down to the approximate middle of Zones 2, 3, and 4. The gases represented approximately the gaseous mixture coming from Zones 3, 4, and 5, respectively.

It was found that the gas composition varied somewhat during different stages of a run, also that the composition was quite different during similar stages of different runs. The carbon monoxide and carbon dioxide content of the gas did not check closely with known equilibrium values for these two gases at this temperature.[7]

This work was not carried far enough to enable us to obtain data which could be regarded as giving absolutely characteristic equilibrium concentrations for the different stages of a run. An average of values obtained during one typical run (after 1 hr. of heating) gave the results recorded in Table III, which were representative of those obtained in a fairly large number of runs.

TABLE III—COMPOSITION OF GAS IN ZONES 3, 4, AND 5

GAS	TOP	MIDDLE	BOTTOM
N	27.1	41.6	61.2
CO	71.3	58.0	38.8
CO_2	1.6	1.4	0.0

Suppose we assume that the reactions occurred as in Equations 1 and 2, we will take then, as a basis for calculation, the changes within the system which would be necessary to account for the appearance of the 6.71 oz. of NaCN and the 2.89 oz. of Fe.

REACTION 1

$6.7 \times 48/98 = 3.29$ oz. carbon necessary
$6.7 \times 106/98 = 7.25$ oz. Na_2CO_3 necessary
$6.7 \times 56/98 = 3.83$ oz. total loss due to reaction or 7.25 (Na_2CO_3 used) + 3.29 (C used) − 6.71 (NaCN formed) = 3.83 total loss due to Reaction 1

REACTION 2

$2.89 \times 48/168 = 0.82$ oz. carbon necessary
$2.89 \times 232/168 = 4.00$ oz. Fe_3O_4 reduced
$2.89 \times 112/168 = 1.93$ oz. total loss due to Reaction 2 or 4.00 (Fe_3O_4 reduced) + 0.82 (C used) − 2.89 (Fe formed) = 1.93 total loss due to Reaction 2

Comparing now the changes calculated with those actually found we have the following:

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[6] Calculations are based upon iron oxide as Fe_3O_4. It is probable that much of the iron was present as Fe_2O_3; this has, however, little bearing on our calculations, inasmuch as the conversion factors are so similar (Fe_3O_4 = 1.38 against Fe_2O_3 = 1.43).

[7] Rhead and Wheeler, *J. Chem. Soc.*, **99** (1911), 1140.

[illegible]	[illegible]	CALCULATED	DIFFERENCE
[illegible]	12.2	[illegible]	4.95 loss
[illegible]	2.01	4.11	2.10 (gain)
[illegible]	4.16	4.00	0.16 (slight loss)

The results of these calculations show a loss of sodium carbonate, a gain of carbon, and practically no change in total iron. (The slight gain indicated is within the limit of experimental error in this determination.)

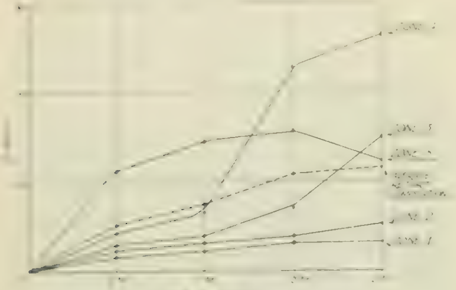

FIG. 2

DISTRIBUTION OF NaCN AND Na_2CO_3

A study of all data shows that at the end of the first half-hour period by far the greatest amount of cyanide (see curve, Fig. 2) had been formed in the bottom of Zone 5 and a progressively decreasing amount in each of the other zones. At the end of the 1-hr. period the same order maintained. At the end of the 1.5-hr. period Zone 4 had the greatest amount of cyanide, Zone 5 next, then progressively decreasing amounts in Zones 3, 2, and 1, respectively. At the end of the 2-hr. period the order of per cent cyanide in the different zones was 4 > 3 > 5 > 2 > 1. From the data it is clearly seen that cyanide formed in the lower zones was distilled upward as the reaction progressed. The total amount of cyanide in the retort at the end of the 2-hr. period was very nearly the same as at the end of the 1.5-hr. period. During this last time interval the rate of distillation from the retort was practically the same as the rate of formation within the reaction zone of the retort.

Although considerable cyanide was distilled up through the reaction zone, the percentage of cyanide in Zones 1 and 2, the two top zones, was at all times low. This was undoubtedly due to the fairly high concentration of CO gas which caused a reversal of the main reaction $Na_2CO_3 + 4C + N_2 = 2NaCN + 3CO$, which resulted at all times in a low concentration of sodium cyanide in the upper zones.

The work of Ferguson and Manning[3] had shown that the presence of carbon monoxide gas has a marked influence on this equilibrium. In their work different amounts of carbon monoxide gas were added to nitrogen, then brought in contact with sodium carbonate, or with sodium cyanide, and the final equilibrium in each case noted.

In Fig. 4, Curves 1 and 2 show the conversion of cyanide obtained by Ferguson and Manning at temperatures of 1000° and 946° C. Curve 3 is the calculated conversion of sodium carbonate to sodium cyanide, obtained at the end of the 1-hr. period as described above, plotted against the average per cent carbon monoxide found in the gas. It should be pointed out that while Curve 3 does not represent true equilibrium conditions, it does, on the other hand, give a good indication of the extent of the reversibility of the main reaction in practice.

TABLE IV—RELATION OF CYANIDE CONVERSION TO GAS COMPOSITION

Conversion of Carbonate to Cyanide[1] Per cent	CO in Gas Mixture Per cent
11.1	71.5
26.0	58.0
55.0	38.8

[1] The amount of Na_2CO_3 and NaCN present at the end of an experiment was taken as the basis of calculation in the determination of per cent conversion of Na_2CO_3 to NaCN. Losses from the retort during the experiment were not included in this calculation.

These results indicate that the equilibrium data obtained by Ferguson and Manning do apply directly to equilibrium conditions as they exist in a large system in which there are present all the materials which take part in the cyanide reaction. They bring out clearly the fact that *producer gas when used at 1000° C. or less would be far less satisfactory than pure nitrogen in this process.* These results show further that in a process using a continuous vertical retort, the greatest conversion of carbonate to cyanide must at all times occur in that part of the heat zone in which nitrogen first enters, *i. e.*, in that part in which the partial pressure of carbon monoxide is lowest.

DISTRIBUTION OF CARBON

During an experiment the concentration of carbon increased in the lower zones. This was due largely to the fact that sodium cyanide (and possibly some sodium carbonate *per se*) had distilled upward from these zones.

The total carbon which disappeared was less than the carbon required for the reactions which have taken place within the retort. This apparent gain in carbon was undoubtedly due to the reaction $2CO = CO_2 + C$. The equilibrium conditions of carbon monoxide would demand some carbon increase; further, the analysis of the gas from the reaction zone showed the presence of carbon dioxide.

DISTRIBUTION OF IRON AND IRON OXIDE

The mixture before briquetting was approximately 50 per cent C, 38 per cent Na_2CO_3, 12 per cent Fe. After addition of water, briquetting, and drying, it was found that practically all the iron had been oxidized and that the composition of the briquets was approximately 48 per cent C, 36.5 per cent Na_2CO_3, 16.5 per cent Fe_3O_4. During the cyanizing process some of the iron oxide was reduced. This reduction was fairly active in the lower heat zones, but in the upper heat zones, 1 and 2, the extent of reduction was exceedingly low, even at the end of the 2-hr. period.

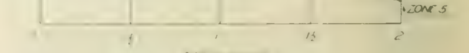

FIG. 3

The equilibrium responsible for the low reduction of iron oxide in the upper heat zones has not as yet been definitely determined. It is now under investigation in this laboratory.

APPLICATION OF RESULTS

The three main points, brought out in this small scale work, which, it seemed, would find direct application in our technical work, were:

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[3] [illegible]

1—The partial pressure of carbon monoxide must be kept as low as possible in order to prevent reversibility of the main reaction. This might be accomplished by keeping the rate of nitrogen flow high enough to overcome (by out-speeding) the effect of the main reaction.

2—Loss of sodium cyanide by volatilization from the lower heat zones should be avoided. This could be accomplished by regulating the length of the retort, the rate of heat conduction through the briquets, and the discharge rate in such a manner as to get a maximum of fixation with a minimum of volatilization. This condition would correspond, in our 4-in. batch retort, to a discharge at the end of the 1.5-hr. period.

3—Temperatures at least as high as 1050° C. should be employed. This temperature is somewhat higher than has previously been used.

LARGE SCALE WORK

Two 8-in. cyanizing retorts 10 ft. in length, of a type similar to those installed in the Saltville plant, were set up and put into operation. A mixer, briquetter, and dryer of sufficient capacity to care for the two cyanizers were also installed.

We at first experienced difficulty in procuring, economically, nitrogen for this work. A simple but surprisingly efficient method was finally worked out whereby nitrogen was obtained by passing air over heated coke. This was a type of low temperature combustion, giving the reaction $C + O + N \text{ (air)} \longrightarrow CO_2 + N$. A retort was constructed of such size (8 in. × 6 ft.) that when air at such a rate as would furnish the required amount of nitrogen (5 to 6 cu. ft. per min.) was passed through the coke, the heat of reaction was just enough to cause the reaction to be self-sustaining (temperature approximately 475° C.). This retort was mounted vertically within a furnace which could be heated by means of an oil burner. The burner was used in starting up the reaction and in bringing up the temperature in case any drop of temperature occurred within the retort. The carbon monoxide formed was removed by a circulating caustic scrubber, and nitrogen of better than 99 per cent purity was obtained (the presence of more than 1 per cent oxygen decreases the nitrogen fixation markedly). This process was run for days at a time and caused but little trouble.

When a cyanizing run was started it was carried on continuously in 8-hr. shifts. The calculated cyanide yield, etc., was based on the average for each 8-hr. period.

The first attempt to cyanize continuously was made on May 27, 1918. Owing to the inexperience of the men and difficulties with the apparatus, the highest fixation recorded during this run was 17.89 per cent sodium cyanide in briquets.

On July 16 another run was started. This run continued for about 12 days, during which time it was possible thoroughly to acquaint the men with their various duties and to correlate chemical and mechanical control. During one shift cyanide in briquets reached 23.17 per cent. The average for the entire period was about 15 per cent.

Following this a number of shorter runs of 3 to 4 days each were made. Over one 40-hr. period of five shifts, briquets with an average of 25 per cent sodium cyanide content were obtained. This gave a cyanide output between 7 and 8 lbs. per retort per hr. This seemed a normal output to expect, inasmuch as we were able to reach and hold this figure.

Later the principles stated under small scale work were more exactingly applied, and every care was exercised to regulate mechanical control so as to conform to rate of chemical reaction.

In the last run made, the following results were obtained:

SHIFT No.	Pounds of Briquets Cyanized	Pounds of Briquets Cyanized per Hr.	Per cent NaCN in Briquets	Pounds NaCN per Retort per Hr.
65	181.6	22.7	35.04	7.95
66	199.2	24.9	36.06	8.99
67	214.4	26.8	32.14	8.63
68	265.6	33.2	31.56	10.47

During another shift of 6 hrs. (No. 71), later in this run, 353.5 lbs. of briquets having a sodium cyanide content of 20 per cent were discharged at the rate of 58.9 lbs. per hr. This gave a production of 12.19 lbs. sodium cyanide per retort per hr. The run was terminated at this point owing to mechanical difficulties in the plant.

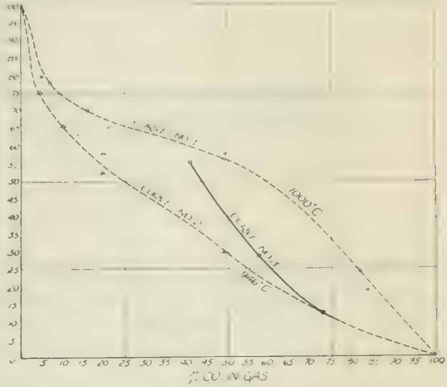

FIG. 4

COST OF AMMONIA PRODUCTION

At the time of the Armistice sufficient progress had been made in the experimental cyanizing work to show that nitrogen could be fixed as cyanide at figures below previous estimates. Conversion of cyanide to ammonia and to nitrates offered no serious difficulties and could be accomplished at a low cost.

Two sets of cost estimates were carefully compiled during August 1918. Calculations were based upon a cyanide-ammonia plant which could produce 5 tons of ammonia per day.

TABULATED SUMMARY OF THE FIGURES OBTAINED, REDUCED TO A NET COST PER POUND OF AMMONIA

	ESTIMATE 1			ESTIMATE 2		
	Based on 7 Lbs. NaCN per Hr., 20 Per cent NaCN, 85 Per cent NH_3. Plant to Cost $2,700,000			Based on 8 Lbs. NaCN per Hr., 23 Per cent NaCN, 95 Per cent NH_3. Plant to Cost $2,100,000		
	3-yr. Amort.	5-yr. Amort.	15 Per cent	3-yr. Amort.	5-yr. Amort.	15 Per cent
Coke reactions	....	0.0324	....	....	0.0284	....
Coke loss and discard[1]	....	0.0022	....	....	0.0019	....
Na_2CO_3, loss and discard[1]	....	0.0036	....	....	0.003	....
Fe loss and discard[1]	....	0.0018	....	....	0.0016	....
Nitrogen	....	0.004	....	....	0.003	....
Steam	....	0.0014	....	....	0.0012	....
Replacement of retorts and equipment, cyanizing	....	0.0663	....	....	0.0526	....
Replacement costs, steaming	....	0.0105	....	....	0.0084	....
Fuel	....	0.0166	....	....	0.0151	....
Power	....	0.0123	....	....	0.0107	....
Labor	....	0.0644	....	....	0.0613	....
Total, excluding fixed charges	....	0.2204	....	....	0.1876	....
Fixed charges	$0.25	0.15	0.1125	0.1445	0.1166	0.0876
Total per lb. NH_3, including fixed charges	0.47	0.37	0.33	0.38	0.30	0.275

[1] Discard due to accumulation of ash during a continuous cyanizing—steaming-cyanizing process.

Estimate 1 was based upon the assumption that one cyanizing retort would be capable of producing cyanized briquets of 20 per cent sodium cyanide content at the rate of 7 lbs. sodium cyanide per hr. and that this cyanide could be converted into ammonia with 85 per cent recovery. This would give 50.4 lbs. of ammonia per retort per day. It would be necessary to keep 198 cyanizing retorts in operation. Estimating the life of a retort as 15 days, 215 retorts would be needed in the installation.

Estimate 2 was based on the assumption that each cyanizing retort would produce briquets of 23 per cent sodium cyanide content at the rate of 8 lbs. sodium cyanide per hr., and with 95 per cent ammonia recovery 158 cyanizing retorts would have to be kept in operation. A total of 170 would have to be installed.

Fixed charges were based upon cost of construction of the government cyanide plant at Saltville,[9] and calculated for amortization of plant (*a*) in 3 years, (*b*) in 5 years, (*c*) 15 per cent annual depreciation. Estimated cost of materials were as follows:

Coal for fuel at	$ 4.00 per ton
Coke (low ash) at	25.00 per ton
Iron at	60.00 per ton
Soda ash at	35.00 per ton

All costs were worked out in detail.

[9] *Loc. cit.*

Preparation of Alpha, Gamma Quinolines—I[1,2,3]

2,4-Dimethyl-6-Ethoxyquinoline: An Improved Method for Its Preparation

By S. Palkin and M. Harris

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The value of the dicyanine dyes for spectrophotographic work and their continued absence from the American markets led to an investigation of the preparation of the quinoline intermediates for these dyes, with a view to developing a commercial process more suitable than those now available and to working out some means of increasing the yields.

The steps involved in the recovery of the pure quinoline derivatives constitute by far the greatest difficulties in the preparation of these α,γ-quinolines, requiring repeated steam distillations or ether extractions. This is in a large measure due to the tar formed in the synthesis.

The method described differs essentially from the former methods in the treatment of the reaction mixtures after the synthesis and the recovery of the pure base.

THE condensation of ethylidene acetone with aniline, discovered by Baeyer,[4] was used, with modifications, by Mikeska, Stewart, and Wise[5] for the preparation of 2,4-dimethylquinoline. By the substitution of *p*-toluidine for aniline in the condensation, Pfitzinger[6] prepared α,γ-dimethyltoluquinoline (or 2,4,6-trimethylquinoline). Using *p*-phenetidine as the primary base in this synthesis, Mikeska, Haller, and Adams[7] prepared 2,4-dimethyl-6-ethoxyquinoline. Very material improvements in the recovery and purification of the quinoline base. Ether extractions were substituted for steam distillation hitherto employed, and acetylation and diazotization were used for the removal of the unchanged primary and hydro base.

SYNTHESIS

The synthesis proper is based on the Baeyer condensation and is carried out as described by Mikeska, Haller and Adams.[7] The reaction product is treated as follows: A current of steam is passed through the reaction mixture (which has been diluted with 2 l. of water) for 0.5 hr. After cooling, the supernatant liquid is poured off and the tarry residue is washed several times with dilute hydrochloric acid which is added to the main solution. The acid solution is treated with an excess of strong sodium hydroxide. When the oil has risen to the top (several hours are required) the aqueous layer is drawn off and the oily base subjected to vacuum distillation (30 to 70 mm). After removal of the water, the oil is collected to about 225° (30 mm.). This "crude base" distillate is treated on the steam bath with an equal weight of acetic anhydride and poured gradually into 3 l. of water. Most of the primary base and the hydro base is thus converted into insoluble acetyl compounds, which are removed by filtration after solidification. The cool filtrate is neutralized

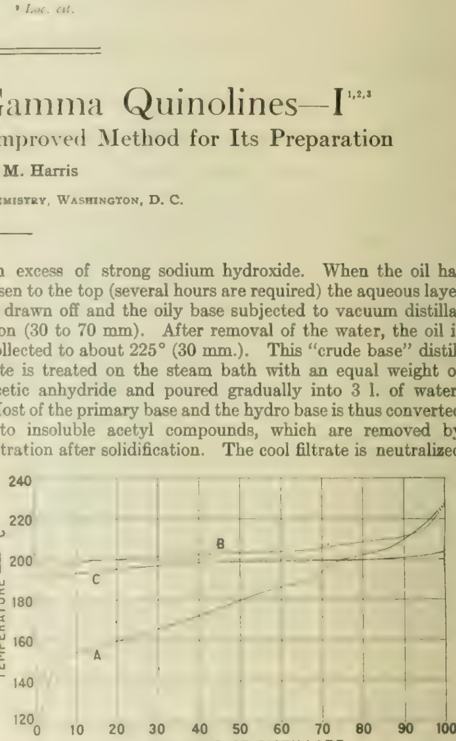

FIG. 1—BOILING RANGES AT 30 MM.
A = crude distillate; B = distillate after acetylation; C = distillate after diazotization

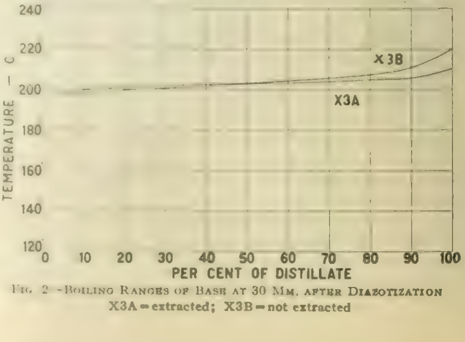

FIG. 2—BOILING RANGES OF BASE AT 30 MM. AFTER DIAZOTIZATION
X3A = extracted; X3B = not extracted

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[1] Received January 18, 1922.

[2] Published by permission of the Secretary of Agriculture.

[3] Contribution No. 56 [illegible] Color Laboratory.

[4] J. prakt. Chem., [illegible]

[5] This Journal, 11 [illegible]

[6] J. prakt. Chem., [illegible]

[7] J. Am. Chem. Soc., 42 [illegible]

with strong sodium hydroxide solution, the solidified base is removed by filtration and dissolved in twice its weight of concentrated hydrochloric acid and the cooled mass is diazotized. Upon dilution of the reaction mixture to about 4 l. with water, all of the base hydrochlorides dissolve, leaving a brown insoluble residue of phenacetin which contains the nitroso compounds. This residue is removed by filtration and a current of steam is passed through the filtrate for about 20 min. to decompose the diazonium salts to phenol. The cooled solution is filtered through cotton and neutralized. The base solidifies as a brown mass in about 1 hr., and is removed by filtration and distilled in vacuum. The base is recrystallized from 800 cc. of hot 18 per cent hydrochloric acid solution, filtered in three stages: *viz.*, when the solution has cooled to 40° to 50° C., to room temperature, and to 0° C. The base is liberated from a water solution with alkali, filtered, and distilled at atmospheric pressure. Nearly the entire product boils between 314° and 316°+. It is almost white in color. The dry crystals melt at 88° to 88.5° C.

PURIFICATION REACTIONS

About 4 k. of "crude base" were prepared. Boiling range curves, determined at 30-mm. pressure, served as a working comparison for the products subjected to subsequent purification.

A portion of this "crude base" was carried through the acetylation purification and vacuum distillation (30 mm.), and boiling range curves were plotted. This distillate served as a working sample for the study of diazotization and the influence of nitroso compounds.

Table I records experiments which were carried out to show the influence of the nitroso compound on the quality of the final base, and to test the feasibility of removing this product by filtration, without resorting to extraction.

TABLE I—EFFECT OF NITROSO COMPOUND ON PURITY OF BASE AND COMPARISON OF FILTRATION AND EXTRACTION AS MEANS OF PURIFICATION

No.	Treatment of Diazotized Mixture	Boiling above 205° C. Per cent	Maximum B. P. at 30 Mm. ° C	B. P. of Recryst. Product at Atmospheric Pressure ° C.	M. P. of Recryst. Product ° C.	REMARKS
X_{3A}	NO compound removed by extraction with ether	15	210	314–316	88.5	Little tar; distillate light in color
X_{3B}	Not extracted	40	220	315–317	Below 88	More tar; distillate dark throughout
AE_1[1]	Filtrate extracted with ether	None	204	314–316	88.5	....
AE_2[1]	Filtrate extracted with ether	None	203	314–316	88.5	....
AE_3[1]	No extraction	None	205	314–316	88.5	....
AE_4[1]	No extraction	None	203	314–316	88.5	....

[1] Insoluble phenacetin with nitroso compound was removed by filtration.

The experiments recorded in Table II were made to determine the optimum conditions for acetylation. Complete removal of primary and hydro base by acetylation alone was not possible in any case.

TABLE II—EFFECT OF VARYING TIME AND TEMPERATURE IN ACETYLATION

No.	Period of Acetylation Steam Bath	"Crude Base" Consumed by Acetylation Per cent	TEST FOR PRIMARY AND HYDRO BASE IN RESIDUE: Residual Phenacetin	TEST FOR PRIMARY AND HYDRO BASE IN RESIDUE: Nitroso Compound by Diazotization
AA	0.5 hr.	53	Present	Present
BB	1 hr.	51	Present	Present
DD	4 hrs.	45	Present	Present
EE	1 day (6 hrs.)	47	Present	Present
FF	2 days (12 hrs.)	49	Present	Present
Y_9	0.5 hr. 129–130°	53 With some tar	Considerable	Considerable

A number of experiments were carried out to determine the effect on the yield and quality of final base of varying conditions of temperature and moisture in the preliminary condensation as well as in the synthesis proper, and the effect of using an oxidizing agent to convert the hydro base to the desired quinoline. The results shown in Table III are self-explanatory.

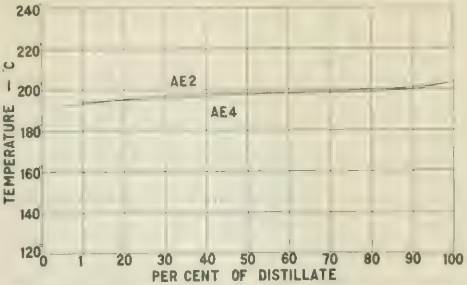

FIG. 3—BOILING RANGES OF BASE AT 30 MM. AFTER DIAZOTIZATION

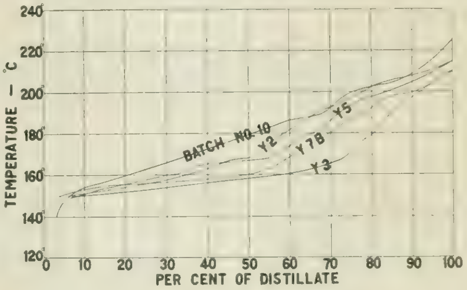

FIG. 4—BOILING RANGES OF "CRUDE BASE"

TABLE III—EFFECT OF VARYING CONDITIONS IN THE SYNTHESIS

No.	Description of Experiment	FRACTION OF "CRUDE BASE" WHICH DISTILS AT 30 MM.: To 160° Per cent	FRACTION OF "CRUDE BASE" WHICH DISTILS AT 30 MM.: 200° Up Per cent	Yield of "Crude" Grams	Yield Pure Base Grams
	Normal				
	Normal as per method average	20	25	(105)[1] 310	(43.4)[1] 86.8
	HCl Saturation-Temperature				
Y_1	Saturated acetone paraldehyde at 10° C.	27.0	19	290	60
Y_2[1]	Saturated acetone paraldehyde at 20° C.	34.0	22	125	21
	Moisture Experiments				
Y_3[1]	Cond. with phenetidine (no water)	57.0	8	106	10
Y_6[1]	Cond. with phenetidine HCl *dry*	22.0	22	150	40.5
Y_5[1]	Saturation with 20 per cent water	29.0	18	130	12
Y_7B[1]	HCl saturation and synthesis carried out same day	50.0	10	122	12.5
Y_8[1]	Used arsenic acid as oxidant	25.0	19	150	30
Y_{10}	Heated "crude base" with arsenic acid	Impossible to	handle—too	much	tar

[1] 0.5 *N* quantities used.

By a bill passed unanimously by the House, the Department of Conservation of the State of Louisiana is given regulatory control over the natural gas fields, to prevent waste and to guarantee a supply of gas to any pipeline that may be built for the distribution of gas. The Department is specifically authorized to curtail the amount of gas used by carbon black mills whenever other markets for domestic or industrial consumption are found.

Jell Strength and Viscosity of Gelatin Solutions[1,2]

By Earle T. Oakes and Clarke E. Davis

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This investigation shows that the solutions of different gelatins bear the same qualitative variations for jell strength with pH.

The form of the jell strength-pH curve is the same for different concentrations.

The maximum for jell strength coincides in pH with the maximum increase in viscosity for aging of solution.

Lack of agreement between viscosity and jell strength may result from differences in the ash content of gelatin.

Viscosity-jell strength measurements properly carried out parallel each other on different gelatins.

The mean molecular weight of gelatin varies directly with the grade and is of the order of magnitude of 1000.

Additional data are submitted in favor of the gelatin-acid combination theory.

A CAREFUL investigation of the viscosities of gelatin solutions indicated that their jell strength would exhibit considerable variation with change in pH, other factors remaining constant. Accordingly such an investigation was undertaken.

Fischer and Coffman[3] have investigated the effects of different acids, bases, and salts on gelatin solutions. Although no pH values are given, we may conclude from their work that gelatin solutions such as were employed by them are liquid in strong acid and strong basic solutions, while they are solid or semisolid in solutions near the neutral point.

Patten and Johnson[4] have continued this work, measuring pH with Clark and Lubs indicators. Although no exact measurements were made of the rigidity of their solutions the following summary indicates their results:

pH	State of Solution at 18° C.
2.8	Liquid
3.6	Semisolid
4.0	Solid
7.9	Semisolid
8.2	Liquid

Sheppard, Sweet and Scott[5] investigated the jell strength of gelatins and glues and described a very accurate form of testing machine. They did not, however, investigate the effect of pH on jell strength.

The method employed by the present authors is essentially one that has been in use for several years in a large gelatin manufacturing concern.[6] As employed by them it has given accurate results when all the conditions have been strictly adhered to. Particular attention must be given to the temperature control, because the jell strength changes enormously with change in temperature. The only difference between the method employed in this investigation and that described below are differences in concentration.

METHOD OF DETERMINING JELL STRENGTH

Weigh into an ordinary glass of about 200-cc. capacity 30 g. of finely ground gelatin. Add 180 cc. of cold water, mix, and let stand 30 min. Heat on a water bath to 60° C., allow to cool to 25° to 30° C., and place in the thermostat at 21° ± 0.1° for 16 hrs. Test the jelly in the testing machine (Fig. 1). This consists essentially of a balance, with a plunger on the right arm, and a platform for supporting a beaker. Suspended from the left arm is a small bucket in which shot are poured to balance the needle at zero when the beaker is placed on the right-hand scale pan. When the glass of jelly is placed on the adjustable platform below the plunger, this is adjusted until the surface of the jelly just touches the plunger when the pointer registers zero. Water is then slowly added to the beaker and the plunger forced into the gelatin until the pointer registers a certain arbitrary value. The number of cc. of water required to bring the pointer to a definite place on the scale (deflection 6) is taken as the jell strength of the jelly. pH measurements were made by means of the hydrogen electrode.

Lipowitz[7] first proposed testing glues with instruments of this type in which the relative consistency of the jelly measured by its capacity for bearing a weight is the underlying principle. Numerous instruments differing in form but not in principle have since been used, not only by manufacturers and buyers but also by scientific investigators.

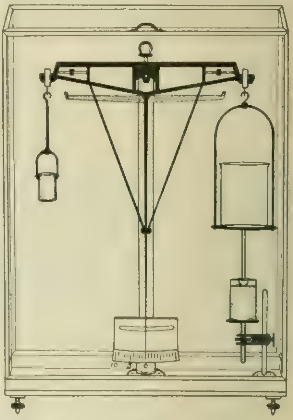

FIG. 1

Smith[8] has described an interesting instrument for measuring jell strength. It consists of a pressure chamber, one side of which is closed with a thin elastic rubber diaphragm, a rubber bulb to produce pressure, and a manometer to measure the pressure produced. Increasing pressure causes the diaphragm to displace the jelly and the pressure required to produce a certain displacement is taken as the jelly strength.

Alexander[9] points out that all methods which depend upon the breaking or compression of the jelly in open glasses are subject to two sources of error. The glasses usually vary in diameter, thus forming a surface of variable area, and there is always a "skin" of greater or less thickness which interferes with the accuracy of the test. To obviate these difficulties Alexander[10] designed a machine to test the resiliency of jelly blocks free from containing walls.

The difficulty arising from employing glasses of varying diameters was overcome in the present case by selecting and employing glasses of the same diameters.

As no data on the "skin effect" were given by Alexander, this point was investigated. Three series of jellies were prepared from Ossein gelatin No. 2. In Series A, the gelatin

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[1] [illegible]

[2] [illegible]

[3] [illegible]

[4] [illegible]

[5] [illegible]

[6] [illegible]

[7] "Neue. Chem. Tech. Unters.," Berlin, **1861**, 37.

[8] *J. Soc. Chem. Ind.*, **28** (1909), 252.

[9] Allen's "Commercial Organic Analysis," 4th edition, **8**, 608.

[10] *J. Soc. Chem. Ind.*, **27** (1908), 459.

solution was left uncovered in the thermostat. In Series B, the surface of the gelatin was covered with toluene after the solution had cooled enough for the jelly to set slightly. In Series C, the surface of the hot gelatin solution was covered by carefully floating toluene over the surface of the solution while it was still hot and before any skin was formed. (In each case the toluene was poured off immediately before the test was run.) The results are given in Table I, Solution 2 being a duplicate of Solution 1 in each case.

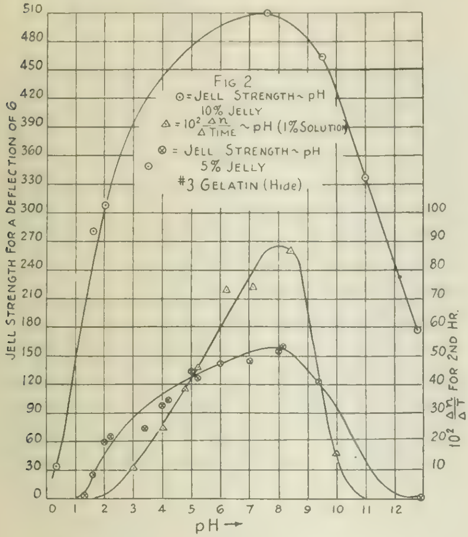


Table I—Jell Strength of 15 Per cent Solution, Gelatin 2

A_1 490	B_1 500	C_1 500
A_2 480	B_2 510	C_2 485

These results not only indicate the reliability of the method when carefully carried out but also serve to show that the skin on the surface of the gelatin had no appreciable effect upon the jell strength. Where the jelly had set beneath the toluene surface the skin could be broken more easily than where no toluene was used, but as will be seen from the results this had no effect upon the jell strengths. Naturally these remarks do not hold for solutions covered with foam which is not removed before the test is run.

Effect of pH on Jell Strength

The jell strength of a 5 per cent solution of hide gelatin (No. 3) was investigated over a range of pH 1.3 to 13.0. The results are plotted in Fig. 2, along with those obtained on 10 per cent solutions of the same gelatin, and show that the jell strength is at a maximum at a pH approximately 8.

Five per cent solutions of No. 2, a low-grade gelatin, and 15 per cent solutions of No. 1, a very low-grade gelatin, gave results in accord with No. 3. No. 1 gelatin was of such low jell strength that solutions more dilute than 15 per cent could not be used because they were liquid over too great a range. In Fig. 2 are also plotted the values for the increase in viscosity during the second hour, as determined by the writers[11] for 1 per cent solutions of the same gelatin at different pH values. The maximum of this curve coincides with the maximum of jell strength and shows that where the viscosity is increasing most rapidly with age of solution the jell strength is also greatest.[12]

Relation between Jell Strength and Viscosity

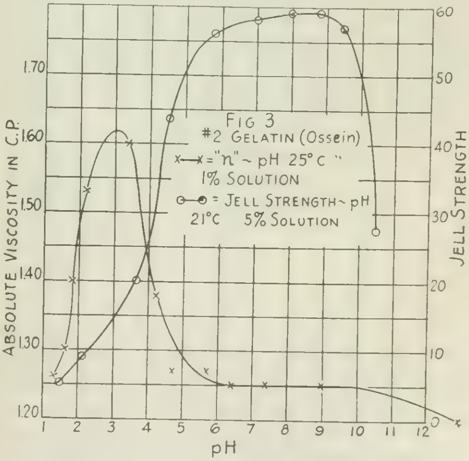
In Fig. 3 the viscosity-pH curve and the jell strength-pH curve for No. 2 gelatin have been reproduced. These curves furnish one reason for the lack of agreement obtained when the same series of gelatins have been classified by viscosity measurements and again by jell strength determinations. Suppose, for example, we select two gelatins exactly alike in every respect, except in their degree of acidity, the pH of Sample A being 8 and the pH of Sample B being 3. A will then give a high jell strength and low viscosity, while B will give a high viscosity and low jell strength. When brought to the same pH they will have the same viscosity and the same jell strength. It is only when a given series of gelatins or glues are tested at the same pH that we can expect to have the classification by viscosity measurements coincide with that for jell strength measurements.

In order to test this relation between jell strength and viscosity more thoroughly, seven samples of gelatin were selected by the manufacturer as samples not classified alike by jell strength and viscosity measurements. Since these samples were not submitted as representative of special kinds of gelatin they were classified as miscellaneous and as such bear the prefix M, so as not to confuse them with the numerals previously employed in designating the kind of gelatin.

Table II

Gelatin	Per cent Moisture	Per cent Ash	Jell Strength 21° C.		Viscosity in Sec., 60° C.
			Mfgr's	Authors'	
M 2	8.16	1.23	600	605	50.2
M 3	7.62	1.03	600	600	51.4
M 1	7.86	0.59	550	550	51.0
M 4	8.10	1.12	450	430	48.1
M 6	7.86	1.04	410	405	47.4
M 5	8.53	0.84	340	330	48.3
M 7	8.33	0.86	310	300	48.0
X	8.93	2.39	59	59	..

Table II gives the jell strength and viscosity values submitted with the samples by the manufacturer as well as jell strength, moisture, and ash obtained by ourselves on the



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[11] Davis, Oakes and Browne, *J. Am. Chem. Soc.*, **43** (1921), 1526.

[12] It must be remembered that it is only possible to use a sterile gelatin for this work. At the pH of maximum jell strength liquefying bacteria develop very rapidly and during the 16-hr. conditioning period may transform an otherwise solid jelly into a viscous liquid.

samples as received. X is a standard low-grade gelatin included for comparison. The gelatins are listed in the order of their jell strength.

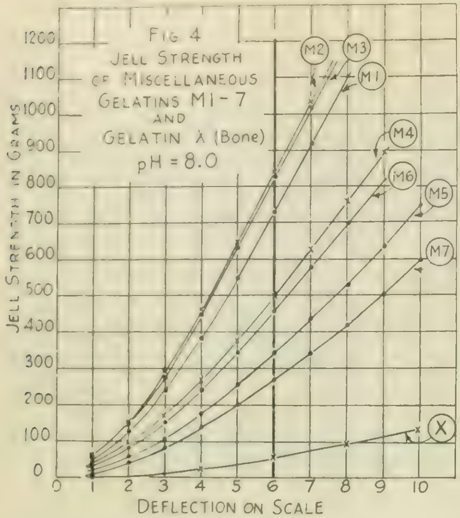
FIG 4
JELL STRENGTH OF MISCELLANEOUS GELATINS M1-7 AND GELATIN X (Bone)
pH = 8.0

The viscosity measurements in Table II were made by the manufacturer and represent the number of seconds required by the hot solution as made up for jelly tests to run through a standard arbitrary viscometer. The jell strengths were determined as heretofore described, and as a check on the manufacturer our jell strengths were determined on the samples without altering the pH, which ranged from 4.0 to 4.4 in the various samples. The results of the two laboratories agree very well on jell strength, but it will be seen that the viscosity values do not parallel the jell strengths.

Since pH exerts such an influence on both jell strength and viscosity it was not expected that the two measurements would grade a set of gelatins alike unless they were made at the same pH. Accordingly these measurements were repeated on all samples at pH 8.0. The jell strengths are shown in Fig. 4, where it is seen that the jellies obey Hooke's law and the lines do not cross.

TABLE III—VISCOSITY AND JELL STRENGTH

Gelatin	Viscosity 1.5 Per cent Solution pH 8.0, Age 3 Hrs., 25° C.	Jell Strength 1.5 Per cent Solution pH 8.0, 21° C.
M 2	3.04	835
M 3	2.96	830
M 1	2.42	720
M 4	1.83	505
M 6	1.68	455
M 5	1.58	350
M 7	1.55	270
X	1.24	59

In determining viscosity the same procedure was employed as previously described.[11] Fig. 5 gives the results for 1.5 per cent solutions at 25° C.; the absolute viscosity in centipoises being plotted against the age of solution. From this figure it is clear that the less the difference between two gelatins the further the age-viscosity curves will have to be prolonged to differentiate between them. These curves are really graphical representations of the tendency of each gelatin to form a jelly, and the viscosity at any age represents a stage in the process ultimately resulting in a solid jelly. It is to be expected, then, that these viscosity measurements and jell strength measurements will parallel each other. The viscosity and jell strength measurements at pH 8.0 are given in Table III, where it is seen that the two determinations classify the gelatins in exactly the same order.

Having demonstrated that at 25° viscosity measurements parallel those for jell strength, it was decided to investigate the causes for the discrepancies in the results when the viscosity was determined at a higher temperature. Since at 40° the viscosity does not change with age and as the thermostat is more easily controlled at 40° than at 60°, the former temperature was selected. The writers are perfectly well aware that the system gelatin-water is quite different at 21° (the temperature at which the jell strengths were determined) from that at 40°. Just what are the differences in the system at these two temperatures is still an open question, but since the differences do exist some chemists have argued that no relation between properties is to be expected. However, it has been repeatedly shown that jell strength and viscosity decrease progressively with the hydrolysis of the gelatin. The greater the mean molecular weight the greater the jell strength and viscosity. It is only in about 25 per cent of the cases that this relation does not hold true and these are precisely the cases that demand attention.

Reference to Table II shows that Samples 2 and 3 and Samples 6 and 5 are the most conspicuous examples of nonconformity to the general rule. These two sets were selected for detailed investigation. Viscosity determinations were made on 1 per cent and 5 per cent solutions of these gelatins at pH 8.0 and 40° C. The results are given in Table IV, and it is seen that they classify the gelatins exactly as in Table II.

TABLE IV—VISCOSITIES OF GELATINS AT 40° C., pH 8.0

Gelatin	1 Per cent Solution	5 Per cent Solution
M 2	0.900	2.817
M 3	0.910	2.884
M 6	0.871	2.465–2.466
M 5	0.879	2.530–2.524

These results establish very clearly the fact that viscosity results above gelation temperatures may not classify gelatins in the same order as do jell strength measurements. In seeking an explanation for these results it was noticed that the gelatins with the abnormally low viscosities had the higher ash content. From the earliest investigations the effect of neutral salts on the physical properties of the proteins has been recognized. Quite recently Loeb[13] has repeated much of this work with various salts but keeping the pH of the solution constant. He has shown that each of the salts normally occurring in the ash of gelatin lowers the viscosity to a marked extent. This is not surprising in view of the fact that these same salts also lower the viscosity of pure water quite as much as they do gelatin solutions, as will be seen from a comparison of Loeb's values for gelatin solutions with those of any of the physical tables for the same salts in pure water. Undoubtedly, then, these abnormally low viscosities are due to the high ash content of the gelatins. To test this by bringing the gelatins to the same ash content it was necessary to ash a quantity of Samples 3 and 5 and to add this ash to solutions of these same gelatins, so that they would have the same ash content as Samples 2 and 6, respectively. The samples could not all be washed to the same ash content for this would change the composition of the sample by removing some of the more soluble, more hydrolyzed, fractions. Not all of the added ash could be dissolved in the gelatin solution, but what did dissolve lowered the viscosity to such an extent as to bring the viscosity measurements at 40° into accord with the jell strength measurements at 21°. The difference in ash content of gelatins is, then, the main cause for the lack of agreement between classifying gelatins by viscosity and jell strength measurements, and for a given ash content viscosity measurements may be substituted for jelly strength measurements. Viscosity measurements may be expressed in absolute units and may be very accurately determined; this is not true of jell strength measurements.

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[13] *J. Gen. Physiol.*, **3** (1921), 391.

ACID AND ALKALI-GELATIN COMBINATION AND THE MOLECULAR WEIGHT OF GELATIN

The behavior of various proteins when subjected to the effects of added acids, bases, and salts has long since been the subject of many investigations.[14] Ostwald and Fischer[15] give an excellent summary of the situation up to that date (1915) in the following paragraph:

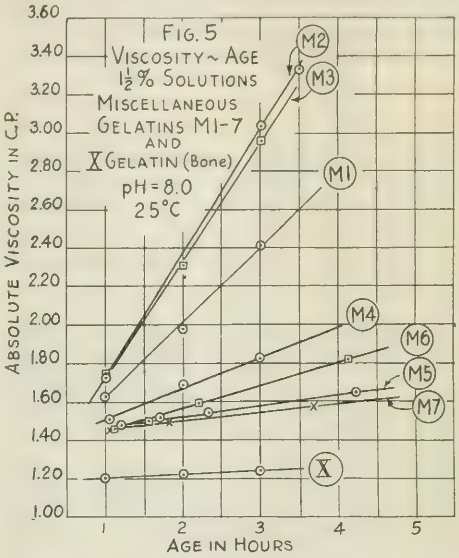
> The most striking fact that the study of the influence of electrolytes on the viscosity of purified proteins has brought out is the enormous change in viscosity which is produced by traces of electrolytes. * * * * * It remains for future investigators to give us a clear and comprehensive presentation of this subject.

This summary of the situation in 1915 is excellent, concise, and accurate. Thanks to Loeb, attention has been directed to activity relationships, and he has studied the effects of different hydrogen-ion concentrations in addition to the effects of different quantities of electrolytes. Although many of Loeb's results are open to different interpretations and therefore many of his conclusions may be unacceptable to other investigators in this field, the fact remains that many of the confusing data have been classified and correlated by considering the effects of different hydrogen-ion concentrations. The implied hope of Ostwald and Fischer is rapidly being attained.

Previous investigators had found maxima in the viscosity-acidity curves and in the viscosity-alkali curves, but since these maxima were at different points for different acids and alkalies no general conclusions could be arrived at. Loeb has shown the existence of a maximum at pH 3.5, regardless of the acid employed. This has been verified by various other investigators, including the authors. In seeking the cause of this maximum the older investigators suggested hydrolysis as the cause of the decline in viscosity after reaching the maximum. Northrup[16] has shown that between the limits pH 2.0 and pH 10.0 the rate of hydrolysis is practically constant. The same thing was found by Davis, Oakes and Browne.[11]

Loeb seeks the explanation for these maxima in the Donnan equilibrium relationship, but his arguments are not entirely convincing.

In experimenting with a number of different grades of gelatin, the authors discovered that the higher grades required less acid to bring them to the point of maximum viscosity at pH 3.5. In fact it was found that a definite relationship exists between the grade of a gelatin and the acid required to titrate it over the range pH 4.7 to pH 3.5. Since there is probably no gelatin that is not made up of a series of the products of hydrolysis of the original tissue, no gelatin can have what may be called a molecular weight. What is determined is the mean molecular weight of all the various fractions making up the gelatin sample. The low-grade gelatins are more completely hydrolyzed and have more of the lower molecular weight fractions. The high-grade gelatins are less hydrolyzed and have a greater mean molecular weight. Among others, Bogue[17] has touched upon this phase. In seeking an explanation for the maximum in the viscosity-pH curve many considerations lead to the conclusion that a compound is formed at this point. The fact that the higher the mean molecular weight of the gelatin the less acid is required to titrate over the range pH 4.7 to pH 3.5 lent considerable support to this view. In order to test this point more thoroughly a number of gelatins of varying grades, and therefore different mean molecular weights, were titrated over this range. In calculating the mean molecular weights from these titration results, the quantity of acid required to titrate pure water over the same range was subtracted from that required by the gelatin and two assumptions were made. One assumption was that the gelatin molecules were monoacidic bases in their combining with acid. The second assumption was that the hydrolysis of the gelatin acid compound was negligible. Neither of these assumptions is justified on the basis of experimental facts, but the results are undoubtedly valuable in showing the variation of mean molecular weight with physical properties. Also these results serve to fix the order of the mean molecular weight of gelatin since neither assumption could account for the differences between 800 and 100,000 as have been obtained by previous investigators. Paal[18] and Procter[19] report a molecular weight of around 840, while Smith[20] obtains a molecular weight around 96,000.



By dissolving 1 g. of gelatin in 99 cc. of water and titrating over the range pH 4.7 to pH 3.5 with 0.2 *M* HCl and subtracting the amount of acid necessary to titrate the same amount of water over this range, the molecular weights were calculated as described above. These values are given in Table V along with the jelly strength of each gelatin.

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[14] Von Schroeder, *Z. physik. Chem.*, **45** (1903), 75; Lewites, *Kolloid-Z.*, **2** (1908), 208; Gokun, *Ibid.*, **3** (1908), 84; Laqueur and Sackur, *Hofmeister's Beitr.*, **3** (1903), 193; Hardy, *J. Physiol.*, **33** (1905), 251; Pauli and co-workers, *Kolloid-Z.*, **3** (1908), 2; **7** (1910), 241; *Biochem. Z.*, **27** (1910), 296; Zoja, *Kolloid-Z.*, **3** (1908), 249; Procter, *Ibid.*, **3** (1908), 307; *J. Chem. Soc.*, **105** (1914), 313; Procter and Wilson, *Ibid.*, **109** (1916), 307; Tolman, *J. Am. Chem. Soc.*, **35** (1913), 307, 317; Tolman and Stearn, *Ibid.*, **40** (1918), 264; Robertson, Van Slyke, Ostwald, and Fischer in their texts and journal articles.

[15] "Handbook of Colloid Chemistry," 170.

[16] *J. Gen. Physiol.*, **3** (1921), 715.

[17] *Chem. Met. Eng.*, **23** (1920), 5, 61, 105, 154, 197.

[18] *Ber.*, **25** (1892), 1202.

[19] *J. Chem. Soc.*, **105** (1914), 313.

[20] *J. Am. Chem. Soc.*, **43** (1921), 1350.

TABLE V—MOLECULAR WEIGHTS OF VARIOUS GELATINS

Gelatin	Jell Strength pH 4.2; 21.0° C.	Cc. 0.2 *M* HCl to Change 1 G. Gelatin from pH 4.7 to pH 3.5	Molecular Weight of Gelatin
X	[illegible]	3.79	1319
2	430	2.85	1753
2 F	565	2.70	1852
3	800	2.48	2016
3 B	1025	2.40	2083

These results, burdened as they are by assumptions as to the monacid character of the gelatin and the absence of hydrolysis of the gelatin acid compound, plainly indicate the order of magnitude of the molecular weight and its progressive increase with the grade of gelatin. Additional evidence is also furnished as to the formation of a compound between the gelatin and the acid. Gelatin at the isoelectric point has a low viscosity. Addition of acid results in the formation of a gelatin acid compound having an increased viscosity. Addition of acid alone to water lowers the viscosity tremendously, a few per cent sufficing to reduce the viscosity to about one-half that of pure water.[21] Consequently, when the gelatin acid combination is complete additional acid exerts its influence and the viscosity is again lowered.

Van Slyke and Van Slyke[22] give an excellent bibliography of work supporting the view of the formation of compounds between proteins and acids and bases.

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[21] Wagner, *Z. physik. Chem.*, **5** (1890), 31.

[22] *Am. Chem. J.*, **38** (1907), 383.

A Study of the Relation of Pectin and Acidity in Jelly Making[1]

By Lal Singh

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Jelly can be prepared from a mixture of pectin, acid, sugar, and water. A definite relation exists between the amount of acid present in fruit juices and the amount of sugar necessary to form jelly. Between certain limits, the greater the acidity of the juice the lower the amount of sugar required. It is therefore desirable to increase the acidity of the juice to the maximum limit compatible with taste, in order to save sugar.

Within certain limits, the higher the percentage of pectin in a fruit juice the lower the amount of sugar necessary to form a jelly. After a certain concentration of pectin in a jelly is reached, any excess remains inactive. By increasing the pectin in a juice from 0.9 per cent to 1.5 per cent, a jelly maker can easily save over 15 per cent of sugar.

It is also noted in this article that the lemon peels which go to waste at citric acid factories would yield pectin at the rate of over 90 lbs. per ton of waste peels.

PECTIN and acid are considered the two necessary constituents of fruit juices in jelly making. It has also long been recognized that juices of high acidity yield firmer jellies than juices equally rich in pectin but deficient in acid. However, no published data are to be found upon the effect of acid concentration upon the jelling quality of citrus juices. Consequently the following series of experiments were conducted in duplicate to determine whether or not any direct relationship exists between the amount of acid present in citrus juice and the jelling point.

EFFECT OF ACID CONCENTRATION

In this series of experiments pure pectin solution, pure citric acid, water, and sugar were used.

To prepare the pectin solution commercial, powdered citrus fruit pectin was leached in boiling water and filtered through felt. Four extractions were made. The resulting dilute pectin solution was concentrated to about one-fourth of its original volume. Triplicate analysis by alcohol precipitation showed this solution to contain 5.5 per cent pectin. A citric acid solution containing 25 g. of acid per 100 cc. was used as a source of acid.

Small (100-g.) lots of jelly were made in which the amount of pectin (1.5 g.) was kept constant. The acid concentration and sugar were varied in a definite and carefully controlled manner in order to determine the effect of acidity upon the jelling point.

For example, in preparing a sample to contain 1.5 per cent pectin, 1 per cent acid, and 60 per cent sugar there were added to 27.3 cc. of pectin solution (equivalent to 1.5 g. of pectin) in a weighed aluminium stew pan, 4 cc. of citric acid solution, 60 g. of sugar, and a small amount of water. The mixture was boiled to dissolve the sugar and to concentrate the solution until it reached a weight of exactly 100 g. It was then poured into a jelly glass, covered to prevent evaporation, and stored for 12 to 24 hrs. to observe whether or not the product formed jelly. In case it jellied the same experiment was repeated with smaller amounts of sugar, *e. g.*, 57, 55, 53, etc., g., successively. If it did not jell, larger amounts of sugar were used successively. By this process of elimination the sugar concentration was determined within 1 per cent for the jelling point at 1 per cent acidity.

In a similar fashion, more than one hundred samples were prepared and the minimum concentrations of sugar necessary barely to form jelly at a number of different acid concentrations were determined. The results appear in Table I and Fig. 1.

TABLE I—RELATION OF ACIDITY AND MINIMUM SUGAR CONCENTRATION TO PRODUCE JELLY PECTIN CONCENTRATION CONSTANT THROUGHOUT THE SERIES AT 1.5 PER CENT

Expt.	Total Acid Present in Finished Product Per cent	Sugar Required Barely to Cause Jelling Grams
1	0.05	75
2	0.17	64
3	0.3	61.5
4	0.55	56.5
5	0.75	
6	1.05	53.5
7	1.3	
8	1.55	52
9	1.75	
10	2.05	50.5
11	2.55	
12	3.05	50
13	3.55	
14	4.05	50

Sugar tended to crystallize out on the surface of jellies in Expt. 1 after about three days; in Expt. 2 after about a week; in Expt. 3 to a very slight extent after about a month. In the other lots this tendency was not observed. This absence of crystallization may be partly due to the hydrolysis of the cane sugar by the high concentrations of acid used,

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[1] Received [illegible]

but is more probably due to the lower sugar concentrations required for jelly formation at the higher acidities.

No jellies of 65 per cent sugar concentration, or higher, showed any tendency to mold, while the jellies with less than 65 per cent of sugar molded in most cases. All of the jellies which tended to mold were those which remained exposed to the atmosphere for about a week. Those which were tightly covered with sterile caps as soon as poured into sterilized jelly glasses gave little evidence of molding even when the concentration was about 55° Balling.

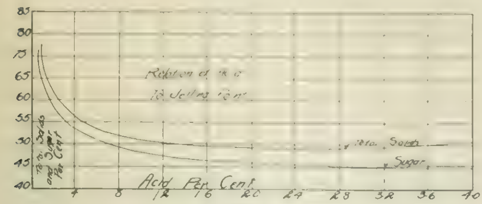

FIG. 1

It would appear justifiable from this experiment to draw the following conclusions:

1—Contrary to the claims made in the literature, it is possible to prepare jelly from a mixture of pectin, acid, sugar, and water even if it is quite deficient in acid.

2—There is a definite relation between the amount of acid present in fruit juice and the amount of sugar necessary to form jelly. Between certain limits, the greater the acidity of the juice the lower the amount of sugar necessary. This relation is very marked, especially when the acidity of the juice is comparatively low. For instance, the sample of 0.1 per cent acidity required 66 per cent sugar to jell, but when the acidity was increased to 0.2, 0.5, and 1 per cent, jelly was formed at 62°, 57°, and 54° Balling, respectively. Thus, by increasing the acidity of the juice from 0.1 to 1.7 almost 20 per cent of sugar was saved. Increase of acidity beyond 2 per cent did not materially decrease the sugar percentage necessary for jelling.

From the viewpoint of the commercial jelly manufacturer, as well as the home jelly maker, it is desirable to increase the acidity of the juice to the maximum limit compatible with the taste of the consumer, in order to economize on sugar. Cull lemons offer a cheap and excellent source of acid either in the fresh juice or for citric acid.

3—If jelly is prepared at sugar concentrations lower than 65 per cent, the container and contents must be pasteurized.

EFFECT OF PECTIN CONCENTRATION

An experiment similar to the one just described was conducted to determine the relation of pectin concentration to the jelling point.

The procedure for this experiment was similar to that adopted for the previous experiments on the effect of acidity upon the jelling point of juice. The concentration of acid was kept constant throughout the experiments while the amount of pectin was varied. The final product in each lot was 100 g. The amount of acid used throughout was 6 cc. equivalent to 1.5 g. of citric acid. The pectin solution contained 5.5 per cent pectin.

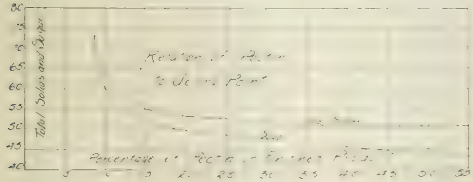

FIG. 2

Various lots of jelly containing 0.5, 0.75, 0.9, 1, 1.25, 1.5, 1.75, 2, 4.2, and 5.5 per cent, respectively, of pectin, based upon the finished product, were prepared, and the minimum concentration of sugar required barely to form jelly in each case was determined. The results are given in Table II and Fig. 2.

TABLE II—RELATION OF PECTIN CONCENTRATION TO JELLING POINT

Pectin in Finished Product Per cent	Sugar Present in Finished Product at Lowest Sugar Concentration for Jelling Per cent
0.5	No jelly formed at any concentration
0.75	
0.9	65
1.	62
1.25	54
1.5	52
1.75	51
2.	49.5
2.75	48
4.2	45
5.5	43

The pectin solution employed in these experiments was prepared by dissolving a commercially prepared powdered pectin in water. Its pectin content was determined by alcohol precipitation and although it contained some impurities the results are at least comparative.

The above experiments show that, within certain limits, the higher the percentage of pectin in the juice the lower the amount of sugar required to form jelly. This fact is most noticeable in jellies containing 0.5 to 1.5 per cent pectin. The curve is very sharp between these two limits, becoming almost horizontal after a concentration of 2.5 per cent pectin is reached.

It also appears that after a certain concentration of pectin is reached in a jelly any excess added remains inactive or undissolved. For instance, it was noticed that all the jellies containing 2 per cent or less pectin were normal and showed no distinct taste of pectin. But when the pectin concentration was raised to 2.75 per cent in the jelly, a crust-like formation appeared on the jelly which was not only stiffer but less sweet than the lower portion of the jelly. This became more and more evident as the concentration of pectin was increased.

This experiment shows how essential it is for a jelly maker to see to it that his juice is rich in pectin, because it will mean a great saving in sugar. For instance, by increasing the pectin in the juice from 0.9 to 1.5 per cent (based on the finished product) a jelly maker can easily save over 15 per cent sugar. Even a saving of 10 per cent of sugar in big commercial factories amounts to thousands of dollars per month.

PECTIN CONTENT OF WASTE LEMON PEEL

In conjunction with this experiment the writer undertook to determine quantitatively the amount of pectin in waste lemon peels which at present largely go to waste at citric acid factories. It was found that waste lemon peels are extremely rich in pectin, 800 g. of peels yielding 37 g. of pure powdered pectin, or at the rate of over 90 lbs. of pectin per ton of waste lemon peels. Consequently the waste lemon peels constitute a commercial source of pectin. The peels can be boiled separately and the extract or purified pectin added to orange juice to supply pectin, or it can simply be added to sliced oranges and boiled with the latter for extraction of juice to make jelly or marmalade.

Carnegie Institute of Technology at Pittsburgh has been selected by the United States Naval Academy to give advanced courses in metallurgy to its graduate officers. Beginning next September, the Academy will send two ordnance officers, graduates of the Academy, for a year's study, which will include graduate work in advanced metallurgy with some studies in electricity and physical chemistry. Other groups of graduate officers are assigned each year to various colleges or universities to study along specialized lines, but Carnegie Institute is the only school chosen for metallurgical instruction.

Moisture Absorptive Power of Different Sugars and Carbohydrates under Varying Conditions of Atmospheric Humidity[1]

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In tests in which dried carbohydrates were exposed to atmospheric humidity (60 per cent), starch showed the greatest moisture absorptive power during the first hour. Next in order came cellulose and agar. Levulose, which is considered by many the most hygroscopic of the carbohydrates, was eleventh on the list. The lowest absorption was shown by dextrose, mannitol, and sucrose.

In a saturated atmosphere, however, the levulose-containing materials showed the highest, mannitol the lowest, absorptive power.

When the samples were allowed to come to equilibrium under ordinary atmospheric conditions after exposure to 100 per cent humidity, all lost moisture except lactose and raffinose, which showed a slight gain for many months. Sugars which absorbed moisture in excess of the monohydrate form lost moisture to the point of monohydration. Sucrose continued to lose moisture during a period of two years

While the absorptive power of the substances studied was highest in periods of high humidity and lowest in periods of lowest humidity, no fixed relationship could be established between percentage humidity and moisture content, owing to the rapidity of atmospheric fluctuations and the lag in the absorptive power of each material.

THE gain and loss in weight of different food materials under varying conditions of atmospheric humidity was the subject of a paper which the author read before the Division of Agricultural and Food Chemistry at the Philadelphia Meeting of the AMERICAN CHEMICAL SOCIETY in 1919. Since then the experiments have been continued with a number of different sugars and carbohydrates, singly and in mixtures, and a few general results of the work are reported in the present paper.

The materials used in the experiments were the sugars dextrose, levulose, rhamnose, sucrose, maltose, lactose, and [illegible] r alcohol mannitol; the polysaccharides [illegible]; the hemicellulose agar; and five com[illegible], a refiner's molasses, a low-grade honey, a maltose sirup, a [illegible].

The substances were first dried in a vacuum oven to constant weight in the presence of phosphorus pentoxide in order to remove all traces of moisture. About 1 g. of the powdered anhydrous material was then spread over the bottom of a weighing bottle, provided with a ground-glass stopper, and exposed to the air. The absorptive power for moisture was measured by weighing the bottles at regular intervals and noting the increase in weight (Table I).

The anhydrous material which showed the greatest absorptive power for moisture during the first hour of exposure was the polysaccharide starch, with 1.04 per cent absorption. This result, while perhaps surprising to many, will not be unexpected by those who have worked with this carbohydrate. Moisture is absorbed from the air by anhydrous starch with so much avidity that heat is evolved. The substances ranking next to starch in absorptive power during the first hour of exposure were cellulose with 0.89 per cent and agar with 0.88 per cent [illegible].

The sugar which is first in absorptive power during the first hour of exposure is anhydrous maltose, with a gain in weight of 0.80 per cent; then follow anhydrous raffinose with a gain of 0.74 per cent, and anhydrous lactose with a gain of 0.54 per cent. The high absorptive power of these sugars shows the necessity of preserving them in hermetically sealed containers.

The substances ranking next in absorptive power are the anhydrous solids of molasses with a gain of 0.46 per cent, honey with 0.44 per cent, glucose sirup with 0.29 per cent, and maltose sirup with 0.28 per cent.

The eleventh material upon the list, with 0.28 per cent absorption, is the sugar levulose, which according to general opinion is the most hygroscopic of all carbohydrates. Pure, dry levulose is not excessively hygroscopic at first. It absorbs moisture slowly but what it does absorb is retained with great tenacity. As the percentage of absorbed moisture increases and the levulose begins to liquefy, the rate of absorption increases rapidly.

The substances of lowest absorption during the first hour of exposure were dextrose with 0.07 per cent gain in weight, mannitol with 0.06 per cent gain, and sucrose with 0.04 per cent gain. The results are all given in the first column of Table I.

The exposure of the substances during the first hour was at a temperature of about 20° and a relative humidity of about 60 per cent. With the varied class of products used in these comparisons some reached moisture saturation before others so that the relative order, at the point where there is no longer any increase in weight, was different than at the end of the first hour. At the end of 9 days a general condition of equilibrium was reached where the percentages of absorbed moisture were found to be as given in the second column of Table I. The average temperature during this 9-day period was 19.6° and the average relative humidity 61 per cent.

TABLE I. PER CENT MOISTURE ABSORBED FROM AIR AT 20° C.

ANHYDROUS MATERIAL	60 Per cent Humidity 1 Hour	60 Per cent Humidity 9 Days	100 Per cent Humidity 25 Days
Starch	1.04	12.98	24.37
Cellulose	0.89	5.37	12.57
Agar	0.88	20.34	42.98
Maltose	0.80	6.97	18.35
Raffinose	0.74	12.90	15.91
Lactose	0.54	1.23	1.38
Molasses	0.46	9.66	68.92[1]
Honey	0.44	10.00	74.10[1]
Commercial glucose	0.29	9.00	47.14[1]
Malt sirup	0.28	8.84	50.96[1]
Levulose	0.28	0.63	73.39[1]
Commercial invert sugar	0.19	5.05	76.58[1]
Rhamnose	0.18	5.00	13.12
Pure invert sugar	0.16	3.00	73.96[1]
Dextrose	0.07	0.07	14.50
Mannitol	0.06	0.05	0.42
Sucrose	0.04	0.03	18.35[1]

[1] Moisture absorption still progressing at end of 25 days.

It will be noted that after 9 days' exposure the hemicellulose material agar showed the highest moisture absorption with 20.34 per cent, starch being second with 12.98 per cent, and raffinose third with 12.90 per cent. Anhydrous raffinose exceeds any other sugar in its absorptive power; the amount absorbed at the end of 9 days is still 5 per cent below the theoretical figure for raffinose pentahydrate. The levulose-containing materials, honey and molasses, had absorbed 10 per cent and 9.66 per cent of moisture, respectively, commercial invert sugar 5.05 per cent, chemically pure invert sugar (made by mixing pure dextrose and levulose in equal proportions) 3 per cent, while pure levulose itself absorbed only 0.63 per cent. Anhydrous dextrose, mannitol, and sucrose are unchanged at the end of the list, having absorbed no more moisture than at the end of the first hour.

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[1] Presented before the [illegible] at the [illegible] Meeting of the American [illegible], April [illegible], 1922.

SATURATED ATMOSPHERE

The experiments thus far conducted were made at the comparatively low relative humidity of 60 per cent, and a new experiment was accordingly made to determine how much moisture the materials would absorb from a water-saturated atmosphere. This was accomplished by placing the products in a closed chamber over water for 25 days; although moisture absorption was still progressing at the end of this time with many of the substances, the experiment was not continued longer owing to the danger of mold formation.

The results of absorption from a saturated atmosphere, shown in the third column of Table I, reveal some very surprising results. The highest absorptive power is no longer held by the insoluble polysaccharides, agar and starch (these materials having reached their saturation point at about the twentieth day), but by the levulose-containing substances. Commercial invert sugar ranks first with 76.58 per cent absorption, honey second with 74.10 per cent, C. P. invert sugar third with 73.96 per cent, pure levulose fourth with 73.39 per cent, and molasses fifth with 68.92 per cent. The presence of levulose has much to do with moisture absorption, but the percentage of water absorbed bears no relation to the percentage of levulose present. Pure levulose, for example, absorbed 73.39 per cent moisture and pure dextrose 14.50 per cent. A mixture of these two sugars in equal amounts might then be expected to have an absorption equal to the average value of 43.95 per cent, but according to experiment this mixture had an actual absorption of 73.96 per cent, which slightly exceeds that of pure levulose. Certain organic and mineral substances may possibly accelerate the moisture-attracting property of levulose, but the mechanism of the process and the formulation of a mixture of highest absorptive power per unit of levulose remain to be worked out.

As to the absorptive power of other sugars at 100 per cent humidity, raffinose absorbed at the end of 25 days 15.91 per cent moisture, which is still about 2 per cent below that necessary to form the pentahydrate; dextrose absorbed 14.50 per cent, which is 4.5 per cent more than necessary to form the monohydrate; rhamnose absorbed 13.12 per cent, which is over 2 per cent more than necessary to form the monohydrate; lactose, the sugar of lowest absorptive power, attracted only 1.38 per cent moisture, which is still less than that necessary to form the monohydrate. The substance of lowest moisture attracting power at 100 per cent humidity was mannitol which, notwithstanding its considerable solubility, gained only 0.42 per cent in weight.

ABSORPTION AFTER EXPOSURE TO 100 PER CENT HUMIDITY

The substances after a 25-day exposure in a moisture-saturated atmosphere were allowed to stand again under ordinary atmospheric conditions until equilibrium was once more reached. The results of approaching this equilibrium from the anhydrous state and from a more or less moisture-saturated state are not, however, identical. All of the products lost moisture upon taking from the moisture-saturated atmosphere, except lactose and raffinose, which continued to show a slight gain for many months. This was to be expected, as these two sugars had still not absorbed the necessary amount of moisture to complete the formation of the stable lactose monohydrate and raffinose pentahydrate. The slowness of final complete absorption in case of these sugars is probably due to occlusion of unchanged anhydride within aggregates of the hydrate. Sugars which had absorbed moisture in excess of the stable monohydrate forms, such as dextrose and rhamnose, lost moisture to this point of monohydration, and there remained practically constant, dextrose with about 10 per cent absorption and rhamnose with about 11 per cent. Maltose also lost moisture after removing from a saturated atmosphere and went back to approximately the monohydrate forms. Levulose decreased from 73.39 to 11.19 per cent, which is slightly above that required for the monohydrate combination.

TABLE II—RANGE IN MOISTURE ABSORPTION DURING THE YEAR UNDER ORDINARY ATMOSPHERIC CONDITIONS FOR MATERIALS PREVIOUSLY EXPOSED TO 100 PER CENT HUMIDITY

MATERIAL	Lowest Per cent	Highest Per cent	Range Per cent
Agar	21.00	30.74	9.74
Raffinose	15.77	16.24	0.47
Starch	12.29	18.41	6.12
Commercial invert sugar	11.81	34.73	22.92
Molasses	11.51	33.00	21.49
Commercial glucose	11.46	23.30	11.84
Malt sirup	11.28	24.36	13.08
Levulose	11.19	36.31	25.12
Rhamnose	10.85	12.29	1.44
Honey	10.52	34.92	24.40
Dextrose	9.88	10.57	0.69
Maltose	5.46	9.37	3.91
Cellulose	5.06	10.89	5.83
Lactose	1.33	1.69	0.36
Mannitol	0.22	0.52	0.30

The range in moisture content of the different materials during the year, after previous exposure for 25 days to 100 per cent humidity, is indicated in Table II. The lowest average interior relative humidity for the climate of New York is about 50 per cent for an average temperature of about 18.5° C. and occurs late in January; the highest average interior relative humidity for this climate is about 70 per cent for an average temperature of about 80° C. and occurs late in July. The general variation in moisture content of the materials studied was a decrease to a minimum in late January and an increase to a maximum in late July.

Of the substances examined, lactose and mannitol showed the lowest absorptive power and the lowest range between minimum and maximum. The substance of highest absorptive power at low humidity was found to be agar with 21.00 per cent water, and the substance of highest absorptive power at high humidity was levulose with 36.31 per cent moisture. In a previous experiment conducted in the summer of 1919, the percentage of moisture absorbed by levulose from the air during a protracted period of rain reached 47.3 per cent (Table V). The average moisture absorptive power of levulose for different months of the year is shown in Table III.

TABLE III—ABSORPTION OF WATER BY LEVULOSE FOR DIFFERENT MONTHS OF THE YEAR

MONTH	ROOM TEMPERATURE ° C.	RELATIVE HUMIDITY	ABSORPTION PER CENT
January	19.5	53.9	13.7
February	19.7	47.5	11.9
March	20.4	56.7	12.8
April	20.6	58.9	13.2
May	21.9	61.8	18.3
June	25.3	71.5	21.2
July	25.7	70.0	28.4
August	24.2	72.1	24.2
September	22.2	71.4	23.2
October	19.9	69.0	22.6
November	20.0	60.1	19.2
December	19.2	56.0	13.5

The experiments of Table II, as previously mentioned, were conducted upon products which had previously absorbed a high percentage of moisture from a saturated atmosphere.

The behavior of sucrose upon removing from this atmosphere is noteworthy. While the other sugars and products came to a condition of equilibrium with the laboratory atmosphere in about 6 wks., the moist sucrose never reached this condition but continued slowly to lose moisture during a period of 2 yrs. The results are given in Table IV.

TABLE IV—LOSS OF MOISTURE FROM WET SUCROSE DURING 2 YRS. ON EXPOSURE TO ROOM ATMOSPHERE

DATE	MOISTURE Per cent	DATE	MOISTURE Per cent
December 17, 1919	18.35	January 1, 1921	7.17
February 1, 1920	11.58	April 1, 1921	6.35
May 1, 1920	10.99	July 1, 1921	4.21
July 1, 1920	9.19	October 1, 1921	2.42
October 1, 1920	7.73	January 1, 1922	1.72

The tenacity of wet sucrose for retaining its moisture is probably due to the occlusion of water within aggregates of crystals which retard evaporation.

While the absorptive power of the substances studied in this investigation was highest in periods of high humidity and lowest in periods of low humidity, no fixed relationship can be established between percentage humidity and moisture content under ordinary conditions owing to the rapidity of atmospheric fluctuations and the inevitable lag in the absorptive power of each material. On a curve of falling and rising humidity two points on the same horizontal can be found of similar atmospheric saturation, but the amount of absorbed moisture in exposed materials at those points is vastly different. This is shown in Table V, which was exhibited at the Philadelphia Meeting in 1919, where various exposed substances were weighed during a period of falling and rising humidity. On July 24 and August 4 the atmospheric conditions as regards temperature and humidity were exactly alike but the percentages of absorbed moisture upon these days varied greatly, the difference in the case of levulose exceeding 28 per cent. This lag, or slowness of adjustment of substance to its equilibrium with the atmosphere, nullifies the attempt to measure atmospheric moisture by the so-called "weight" hygrometer, in which a pointer is moved by the gain or loss in weight of some hygroscopic substance such as gelatin.

TABLE V—SHOWING INFLUENCE OF LAG UPON MOISTURE ABSORPTIVE POWER

	FALLING HUMIDITY		RISING HUMIDITY	
MATERIAL	[illegible] Humidity Per cent	July 24 25° C. 70% Humidity Per cent	August 4 25° C. 70% Humidity Per cent	August 8 26.1° C. 82% Humidity Per cent
Levulose	47.3	46.8	18.5	31.8
Agar	29.7	29.4	23.3	26.3
[illegible]	25.0	24.6	18.9	21.1
[illegible]	21.0	20.9	11.5	14.5
[illegible]	17.8	17.2	10.9	13.6
Cellulose	9.3	8.9	6.2	7.6
Sucrose	0.4	0.3	0.1	0.2

The moisture absorptive power of the sugars and other carbohydrates has many practical bearings. There is first the question of chemical dealers and manufacturers preparing sugars only in the most stable form. Raffinose, for example, should never be prepared for trade purposes as the anhydride but as the stable pentahydrate. There is, second, the question of the legal standard for moisture in certain carbohydrate food products. The maximum permissible moisture content of starchy foods, such as flour, is a point about which there is considerable difference of opinion. There is, third, the question of the best means of preventing farinaceous foods, such as cake, from drying out. Levulose sirup has been proposed as the best anti-desiccating agent. But the experiments show that ordinary invert sugar and honey are equal to levulose in moisture absorptive power. There is, fourth, the important physiological question of the retention of moisture by seeds, bulbs, tubers and the growing parts of plants during germination or in periods of drought. It is here, no doubt, that the hemicelluloses, of which agar is a type, play an important function as moisture holders. These are only a few of the many practical bearings which underly the subject of the moisture absorptive power of the sugars and carbohydrates.

What Next in Europe?

By H. W. Jordan

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The increasing literature of commonsense about economics is an indication of passage from the acidity of war to the alkalinity of sweet harmony, with a reaction that will precipitate ultimate payment by Europe of our war loans.

The authors are not visionary dreamers or chemists out of a job. For instance, Frank A. Vanderlip of the National City Bank, New York, in his book "What Next in Europe?" makes a financial, engineering analysis of the European situation as it relates to American welfare and shows that we must sink or swim intellectually and industrially with Europe.

Discussing labor, he says, "The new attitude of labor appears to me to be perhaps the most promising element in the European outlook. I have been universally well impressed with the grasp of economic principles which these men have shown and with their intellectual ability to argue their case. Europe is sharply awake to the horrors that come upon innocent industrious people, who are highly specialized in their craftmanship and can live only by the exchange of their products, if the whole machinery of international exchange is thrown into confusion by war."

He proposes a plan of rehabilitation under American direction which would result in ultimate payment of our eleven billions loaned Europe; a plan that would furnish abundant employment for many years to our engineering industries and that would be vividly attractive to American technical men, since it would yield a new southeastern Europe quite like industrial America. He would establish great scientific laboratories which "through stimulation of technical education and scientific investigation would give the world new knowledge of incalculable value. The expenditure should be made with great vision of the future, rather than as a palliative to ease the distress of the moment."

"The war has made a great awakening in millions of dormant minds. It is possible that newly awakened impulses, if they can only be harnessed up to the machinery of production and distribution, can result in great actual improvement of civilization."

Mr. Vanderlip's supreme recognition of the part that engineers can play in rehabilitation is epitomized in his conclusion that "if administration of the whole project of expenditure were placed in the hands of a Commission, headed by Herbert Hoover, I think we could all safely go about our domestic affairs and find nothing but satisfaction as we read the report of the work."

The members of the Committee of the League of Nations on International Coöperation in Intellectual Work include in the sciences: Mme. Curie; Prof. Albert Einstein; Miss Bonnevie, professor of zoölogy at Christiania; Dr. A. De Castro, of the medical faculty of the University of Rio de Janeiro; and Dr. L. De Torres Quevedo, director of the electromedical laboratory of Madrid. The commission will include a consideration of the following topics: possibilities of encouraging and improving the organization of scientific research by means of congresses, commissions, and institutes; the international relations between universities and means for the organization of an international bureau of universities and possibly an international university; and international organization of scientific bibliography and exchange of scientific publications.

The Change in Viscosity of Oils with the Temperature[1,2]

By Winslow H. Herschel

U. S. Bureau of Standards, Washington, D. C.

There is no satisfactory theoretical equation for change of viscosity with the temperature.

Of the empirical equations which have been used, the four-constant equation of Bingham has been found most suitable for definite chemical compounds of low viscosity. The three-constant equation of Slotte, in various forms, has proved most serviceable for oils of comparatively high viscosity.

The graphical method of Oelschläger may be considered as based on a two-constant equation, simplified from Slotte's equation, and which gives straight lines on a logarithmic diagram. Oelschläger should have used absolute viscosity instead of the "viscosity factor" calculated from the incorrect Ubbelohde formula. Oelschläger's assumption that logarithmic viscosity-temperature graphs are straight lines is sufficiently accurate for practical purposes, or within the limits of accuracy of commercial viscosimetry, if only oils of medium viscosity are considered, excluding spindle and airplane motor oils, as well as fatty, compounded and unrefined oils.

The viscosity-temperature graphs meet approximately at a point, provided all oils are of the same base, and that the oils are limited as just mentioned.

It is preferable to calculate the point of intersection with the help of a diagram in which the slope of the logarithmic graph is plotted against the logarithm of the absolute viscosity at a standard temperature.

The equation for change of viscosity with the temperature may be used to calculate the temperature of average viscosity, but it is sufficiently accurate to take this temperature as equal to the highest temperature minus one-third the range of temperatures.

Importance of Small Temperature Coefficient of Viscosity for Lubricating Oils

It is well known that an oil will "thin out," or grow less viscous, as the temperature increases, but the theoretical law for the change of viscosity with the temperature is unknown and empirical methods must be employed. The change of viscosity with the temperature, or temperature coefficient of viscosity, is different for different oils. It is less for paraffin than for naphthene base oils and less for fatty than for petroleum oils from any crude, castor oil however being an exception to this rule. From a practical point of view, a small coefficient is desirable for a lubricating oil because it lessens the danger of seizure when the temperature of a bearing is accidentally increased above its normal running value. It is noteworthy that the one characteristic emphasized by German engineers, in discussing possible substitute lubricants, was the temperature coefficient of viscosity.[3]

Need of Estimating Change of Viscosity with the Temperature

Standard temperatures[4] have been adopted in commercial viscosimetry, and estimates would be avoided by their use, but nevertheless it is often necessary to estimate the viscosity of an oil at one temperature from the known viscosity at another. The word estimate is used advisedly, because the relation between viscosity and temperature is not accurately known, two deliveries of oil are seldom identical, and there is always a possibility that impurities will be present which exert an influence upon the temperature coefficient of viscosity. Thus there is need of the method of estimation suggested in this paper, rather than of a table, equation or diagram for each oil. An examination of the equations which have been used elsewhere will indicate the basis of the method of estimation finally used.

Empirical Equations Expressing Fluidity-Temperature Relations

If Saybolt viscosity (the time of flow of oil when measured by means of the Saybolt Universal viscosimeter) is plotted against temperature, as in Fig. 1, a series of more or less hyperbolic curves is obtained, which are inconvenient for extrapolation. Little is gained by using viscosity in poises, the c. g. s. unit of viscosity, as in Fig. 2. It is desirable to adopt a method of plotting, or form of equation, which will give fairly straight lines with as great a variety of liquids as possible.

EQUATION WITH TWO CONSTANTS, USING FLUIDITY—The range in viscosity between the most fluid and the most viscous petroleum products is so great that equations which are suitable for showing the viscosity-temperature relation of lubricants are not equally convenient for gasolines. For the latter, petroleum products with a viscosity less than that of water, it is most convenient to use the equation

$$\text{Fluidity} = \frac{1}{\mu} = A + Bt \qquad (1)$$

Dean and Lane[5] suggest a somewhat similar formula, but use kinematic viscosity (absolute viscosity in poises, divided by the density in g. per cc.) instead of absolute viscosity, with temperatures presumably in ° C., and find that "if the reciprocals of the kinematic viscosities as ordinates are plotted against the temperatures as abscissas, the resulting lines are straight for the lighter fractions and only slightly curved for the heavier fractions."

Fig. 3, partly from data of Thorpe and Rodger,[6] shows fluidity-temperature graphs for some of the aliphatic hydrocarbons and other very fluid liquids. Graphs for commercial gasoline and its substitutes lie between those for water and octane, while aviation gasolines lie between heptane and hexane. It will be noted that the graphs are much straighter

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[1] Received March 2, 1922. Presented before the Section of Petroleum Chemistry at the 63rd Meeting of the American Chemical Society, Birmingham, Ala., April 3 to 7, 1922.

[2] Published by permission of the Director, U. S. Bureau of Standards.

[3] *Z. Ver. deut. Ing.*, **59** (1915), 478.

[4] The standard temperatures in the United States are 100°, 130°, and 210° F. (37.8°, 54.4°, and 98.9° C.), but use is also made of 104°, 131°, and 212° F. (20°, 55°, and 100° C.) which has the advantage of avoiding decimals. See *Proc. Am. Soc. Test. Materials*, **15**, I (1915), 280; **19**, I (1919), 730.

[5] This Journal, **13** (1921), 779.

[6] E. C. Bingham and J. P. Harrison, *Z. physik. Chem.*, **66** (1909), 12; calculated from data of T. E. Thorpe and J. W. Rodger, *Trans. Roy. Soc. London*, **185** (1894), 397; Winslow H. Herschel, *Bur. Stds., Technologic Paper* **125** (1919), 17.

than in Figs. 1 and 2, and that their curvature decreases as the viscosity decreases. Yet even with pentane there is a slight divergence from the straight-line relation indicated by Equation 1.

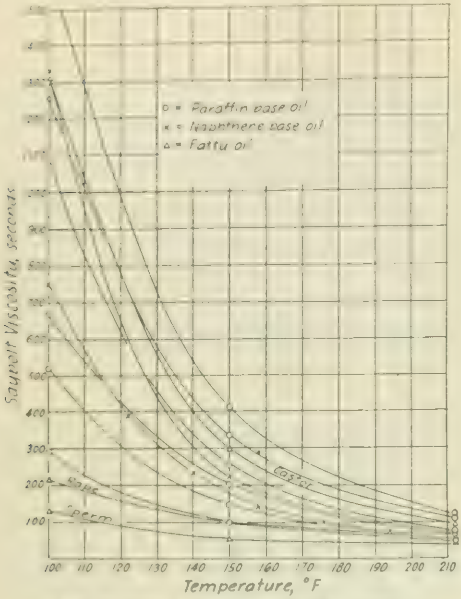

FIG. 1—SAYBOLT VISCOSITY-TEMPERATURE DIAGRAM

It is convenient to use diagrams of the form of Fig. 3 for extrapolation, but care should be taken not to extrapolate beyond the boiling point of the liquid in question. In estimating fluidities at temperatures which are too low to be conveniently reached in testing, it is assumed that the fluidity at the point of solidification, or "pour test," is zero, and then the graph is extended to pass through this point, as shown for one of the samples of kerosene. Water is an exception, because it undergoes a sudden change in consistency when it freezes, instead of gradually growing more viscous, as is the case with mineral oils.

BINGHAM'S EQUATIONS FOR FLUIDITY-TEMPERATURE RELATION—Bingham's belief that fluidities are additive naturally led to his use of fluidity-temperature equations, which have proved applicable to definite chemical compounds of low viscosity.[7] Of special interest are his equations for three of the liquids shown on Fig. 3, hexane, octane, and water. For hexane he found the equation

$$t = 0.[illegible]\phi - \frac{9[illegible].8}{\phi} + 254.0[illegible] \qquad (2)$$

where t is the temperature in °C., and ϕ is the fluidity; for octane,[8] he found

$$T = [illegible] - \frac{[illegible]}{\phi} + \frac{1325100}{\phi^2} \qquad (3)$$

where T is the absolute temperature (°C. + 273). The equation for water[9] is a four constant equation of somewhat similar form to Equation 2:

$$t = 0.23275\,(\phi + 120) + 8.435 - \frac{8676.8}{\phi + 120} \qquad (4)$$

According to Dunstan and Thole, the form of Equation 3 has been found more accurate than that of Equation 2 to reproduce fluidity data obtained by experiment, but it is not as accurate as the form of Equation 4 which also contains four constants.

It is generally considered that the more constants there are in an empirical equation the more accurately it may be made to fit a series of observed points, but Karl Pearson has remarked that a curve based on too great a number of constants may follow the undulations due to experimental error, instead of taking a course which is both smoother and more nearly correct. However, the excessive amount of labor involved is ordinarily a sufficient guard against the use of too many constants.

In the case of petroleum oils, where constants would have to be determined for every brand, it is evident that the uniformity of a given brand is not sufficient to warrant excessive accuracy. There is also considerable doubt as to what form of equation best applies to oils of high viscosity, as the equations above referred to have never been used for very viscous liquids.

SLOTTE'S FORMULA—Thorpe and Rodger,[10] after a thorough examination of available formulas, concluded that Slotte's formula

$$\mu = \frac{\mu_0}{(1 + \beta t)^n} = \frac{c}{(a + t)^n} \qquad (5)$$

gives the best results. Equation 5, when expanded on the

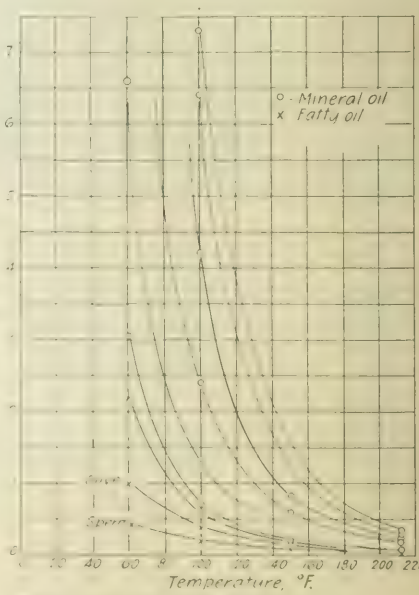

FIG. 2—ABSOLUTE VISCOSITY-TEMPERATURE DIAGRAM

assumption that the temperature coefficient is small, simplifies to

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[7] A. E. Dunstan and F. B. Thole, "The Viscosity of Liquids," 1914, 27.

[8] E. C. Bingham, [illegible] 43 [illegible], 302. Other equations for octane and other [illegible] are given by Dunstan and Thole, Loc. cit., 5.

[9] E. C. Bingham, *Bur. Stds., Sci. Paper* **298** (1917), 75.

[10] *Trans. Roy. Soc. London*, **185**, II (1894), 438; K. F. Slotte, *Beibl. Ann. Physik*, **16** (1892), 182.

$$\mu = \frac{A}{1 + at + bt^2} \tag{6}$$

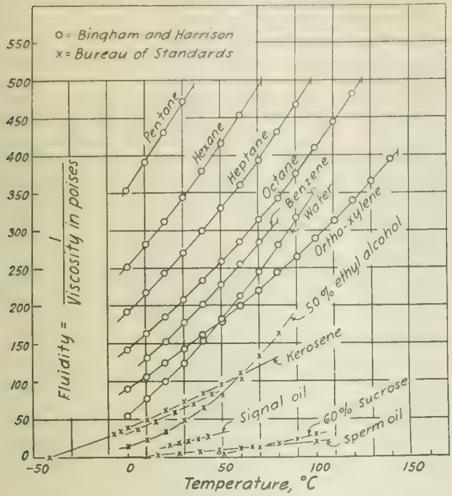

FIG. 3—FLUIDITY-TEMPERATURE DIAGRAM

The work of Dean and Lane is based on Equation 6, modified by substituting kinematic for absolute viscosity. They say, "This is in effect the Slotte equation, which is usually employed to indicate the relation between absolute viscosity and temperature, but which the authors have found equally useful as applied to kinematic viscosity." This method has the advantage that kinematic viscosity is obtained directly from readings of most efflux viscosimeters, while to obtain absolute viscosity it is necessary to determine density (by a hydrometer or otherwise) and make a further calculation.

If Equation 5 is written

$$\mu = \frac{K}{(t - A)^n} \tag{7}$$

where K, A, and n are constants for a given oil, and t is the temperature, it is equivalent to several of the simpler equations which have been proposed. If $n = 3$, t is taken in ° C., and $A = -273$, Equation 7 is equivalent to Batschinski's formula.[11] If $n = 1$, Equation 7 takes the form of Hersey's[12] Equation 49, where "A is the apparent solidifying temperature."

A similar equation was found by Ellis,[13] who found that, "if temperatures be taken above the point of solidification of the oil, and viscosities be taken with reference to the viscosity of water, then (representing temperature by T and viscosity by V) $TV^n = \text{constant}$." Bingham[14] also makes the viscosity-temperature equation depend upon the solidifying temperature, since he regards fluidity as a function of the "free volume," *i. e.*, the volume in excess of that at the temperature at which the fluidity is zero.

SIMPLIFIED SLOTTE EQUATION WITH TWO CONSTANTS

If A in Equation 7 is zero,

$$\mu = \frac{K}{t^n} \tag{8}$$

which represents a straight line on a logarithmic diagram. Since such straight-line diagrams have been used by Oelschläger[15] it is of interest to examine his work and to determine what justification there is for thus simplifying the Slotte equation.

OELSCHLAGER'S METHOD—Oelschläger has given equations and diagrams for estimating the viscosity of oils at different temperatures, but his whole work is based on the unfortunate assumption that Ubbelohde's equation for the Engler viscosimeter is reliable. In reality the error in this equation is about 20 per cent at certain viscosities.[16]

Oelschläger, following Ubbelohde, uses Z to denote the "viscosity factor" which is equal to the kinematic viscosity of the oil, divided by the absolute viscosity of water, in poises, at 0° C. Using a logarithmic diagram, he plots Z, as obtained from Ubbelohde's equation, against the temperature in ° C., and obtains a series of straight lines, one for each oil, which intersect the axis of abscissas (where $Z = 1$, the viscosity factor of water) within a fairly narrow range of temperatures. Taking the average temperature, t_1, at the point of intersection as 185° C. (365° F.), he says that for most oils deviations from this value may be regarded as within the experimental error. Then in order to find the viscosity of an oil at any temperature, t, when its viscosity at 20° C. (68° F.) is known

$$\frac{\log Z}{\log Z_{20}} = \frac{\log t_1 - \log t}{\log t_1 - \log 20} \tag{9}$$

from which

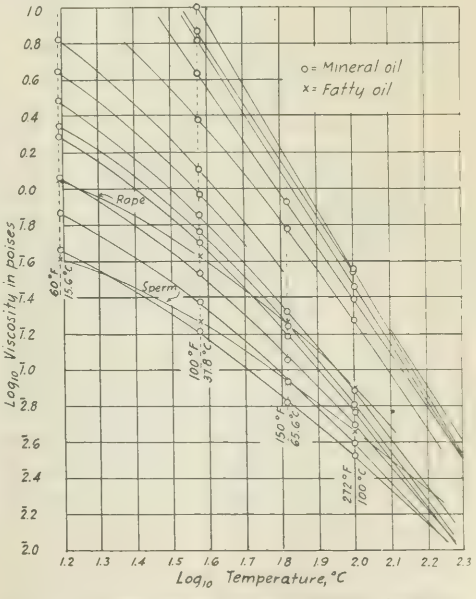

FIG. 4—LOGARITHMIC VISCOSITY-TEMPERATURE DIAGRAM, CENTIGRADE SCALE

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[11] *Proc. Am. Soc. Test. Materials*, **14**, II (1914), 583.

[12] M. D. Hersey, *Trans. Am. Soc. Mech. Eng.*, **37** (1915), 190.

[13] R. L. Ellis, paper presented before the Alabama Light & Traction Association, November 1913. *Met. Chem. Eng.*, **10** (1912), 546.

[14] *J. Am. Chem. Soc.*, **36** (1914), 1391.

[15] *Z. Ver. deut. Ing.*, **62** (1918), 422.

[16] Winslow H. Herschel, *Bur. Stds., Technologic Paper* **100** (1917), 9, 27.

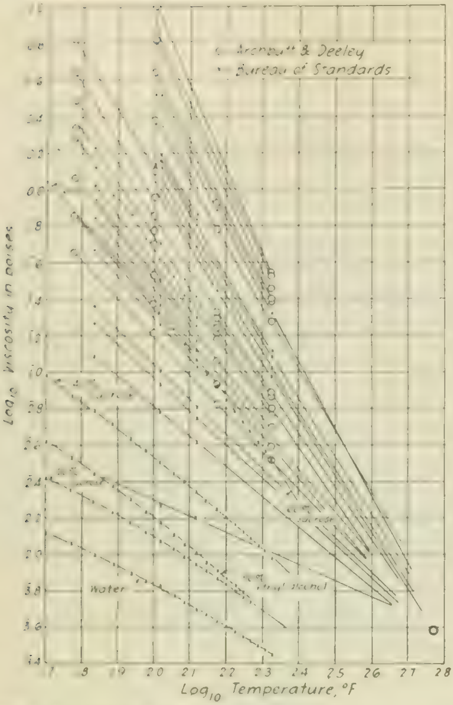

FIG. 5—LOGARITHMIC VISCOSITY-TEMPERATURE DIAGRAM, FAHRENHEIT SCALE, FOR PARAFFIN BASE OILS

$$\log Z = \log Z_{20} \frac{2.267 - \log t}{0.966} \qquad (10)$$

where Z_{20} is the viscosity factor at 20° C. (68° F.).

Oelschläger warns his reader that his method should be used only within the range of temperatures covered by his tests, 20° to 100° C. (68° to 212° F.), and that the value of t_1 is only approximate. One steam engine oil gave 210° C. (410° F.) and another lubricating oil gave 200° C. (392° F.). According to his diagram, the lowest value of t_1 obtained with any mineral lubricating oil was about 175° C. (347° F.).

Both the well-refined oils procured before the war, and the "present deliveries of badly refined oils," showed the straight-line relation, which was also found to hold good for rosin oil. On the other hand, "Oils such as paraffin oil, linseed oil, rapeseed, castor, and sperm, of which only the last two come under consideration as lubricants, act similarly to mineral oils, but the lines are not entirely straight, curving downward somewhat at the higher temperatures. This is especially the case with rapeseed oil, which shows a strongly curved line which is considerably flatter than those for mineral oils at low temperatures."

Two tar oils and three other substitutes for lubricating oils showed straight graphs and low values of t_1. The lowest value, 54° C. (129° F.), was obtained with a transformer oil, supposed to be pine oil, which gave a slightly curved graph, and was the least viscous oil which Oelschläger investigated.

According to Oelschläger, if viscosities are expressed in poises and temperatures in ° C., logarithmic graphs drawn as before will intersect on the line parallel to the axis of abscissas, where the viscosity is 0.0162 poise. As seen from Fig. 4, plotted from data of Archbutt and Deeley[17] the graphs are not straight, except for a few steam engine cylinder oils, and they do not intersect at a point. It is believed that the approximate straightness of Oelschläger's graphs is due to his use of a shorter range of temperatures, and to an entirely accidental balancing of the errors due to the use of the Centigrade scale and of the inaccurate formula of Ubbelohde. As will be shown later, the graphs are approximately straight when the solidification point of the oil is near the zero of the temperature scale which is used in plotting. Thus the Fahrenheit scale gives straighter graphs for the lighter oils, but as shown in Fig. 4, the Centigrade scale gives straighter graphs for very heavy oils. Changing the temperature scale is equivalent to changing the value of A in Equation 7.

It will be noted in Fig. 4 that the curvature of the graphs for rapeseed and sperm oil is greater than for the mineral oils, which is in accordance with Oelschläger's tests.

THE LOGARITHMIC VISCOSITY-TEMPERATURE DIAGRAM, USING FAHRENHEIT DEGREES—Fig. 5 is similar to Fig. 4 but temperatures are in ° F. instead of ° C. It will be noted that a practically straight-line diagram for oils of medium viscosity has been obtained simply by changing the temperature scale. Excluding spindle oils, and those of lower viscosity, and also steam engine cylinder, or airplane motor oils, the graphs for the other oils meet approximately at a point.

The accuracy of the assumption that the graphs of Fig. 5 are straight was investigated as follows. If the viscosities

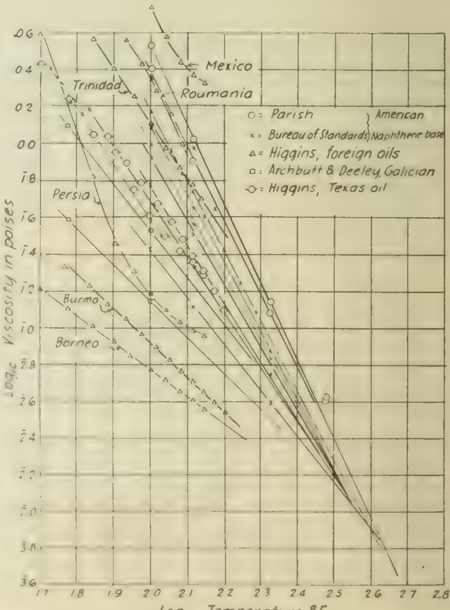

FIG. 6—LOGARITHMIC VISCOSITY-TEMPERATURE DIAGRAM FOR NAPHTHENE BASE OILS

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[17] "Lubrication and Lubricants," **1912**, 190.

$\mu_1\ \mu_2\ \mu_3 \ldots \mu_x$ of a given liquid are known for three or more temperatures $t_1\ t_2\ t_3 \ldots t_x$ the value of n in Equation 7 may be obtained from the equation

$$n = \frac{\log \mu_1 - \log \mu_2}{\log(t_2 - A) - \log(t_1 - A)} = \frac{\log \mu_2 - \log \mu_3}{\log(\mu_2 -)A - \log(\mu_3 - A)}$$

$$= \frac{\log \mu_3 - \log \mu_4}{\log(t_4 - A) - \log(t_3 - A)}, \text{ etc.} \qquad (11)$$

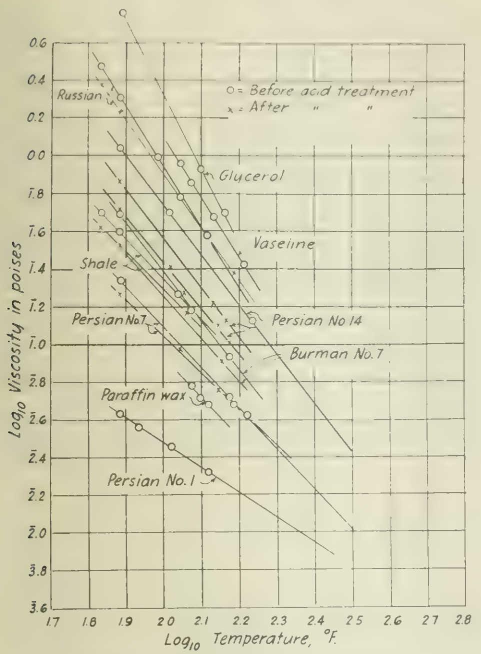

FIG. 7—OILS BEFORE AND AFTER ACID TREATMENT

which may be abbreviated to $n = B = C = D$. From the data of Archbutt and Deeley, for fatty and for American petroleum oils, values of the constants of Equation 7 were obtained, as given in Table I. Temperatures were taken in ° C., and A was chosen by trial so as to give the same value for B and C or for C and D. The temperatures were $t_1 = 15.6°$, $t_2 = 37.8°$, $t_3 = 65.6°$, and $t_4 = 100°$ C. (60°, 100°, 150°, and 212° F., respectively).

TABLE I—CONSTANTS IN EQUATION $\mu = \frac{K}{(t - A)^n}$ FOR FATTY AND AMERICAN PETROLEUM OILS

	VISCOSITIES TAKEN AT TEMPERATURES ° C.					
	15.6, 37.8, and 65.6			37.8, 65.6, and 100		
KIND OF OIL	A	n	K	A	n	K
Sperm	–52	2.88	78000	– 4	1.53	57
Olive	–41	2.97	162000	–25	2.44	9180
Rapeseed	–36	2.72	50000	–36	2.72	50800
Castor	..	....	......	–16	3.62	5020000
Spindle 885	–31	2.64	11500	– 1	1.66	70
Spindle 860/70	–37	3.19	224000	– 3	1.94	314
Light machinery 900/7	–40	3.57	1930000	– 3	2.10	824
Solar red engine	–34	3.65	2950000	– 5	2.39	3930
Bayonne engine	–37	3.78	6920000	–16	2.87	53000
Medium (dark) machinery	–23	3.22	391000	–14	2.82	48100
Valvoline filtered cyl.	..	....	......	–17	3.37	1740000
Dark cylinder A	..	....	......	0	2.94	190000

The average of the fourteen values of A for the petroleum oils is found to be –18.6° C. (–1.5° F.). Using the Fahrenheit scale is therefore equivalent to using almost exactly the correct value of A, since it is the same as using the Centigrade scale with A equal to –18°.

Table II shows the ratio between viscosities as found by experiment and as calculated from the constants of Table I, and shows that the percentage error in Equation 7 is much greater than would be concluded from an inspection of Fig. 5. The oils are in the same order as in Table I, omitting castor oil and the last two petroleum oils.

Assuming no error in viscosimetry, the tables show that n in Equation 7 is slightly greater at low temperatures than at high, except in the case of rapeseed oil, and that it is better to estimate viscosities at high temperature from known viscosities at low temperatures than vice versa.

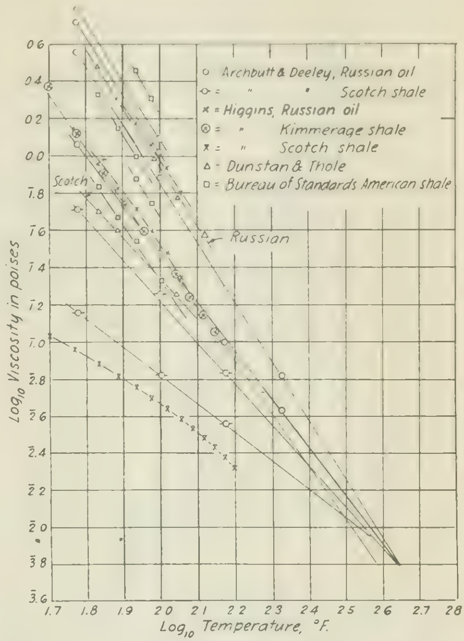

FIG. 8—RUSSIAN, SCOTCH, AND OTHER OILS

TABLE II—RATIO BETWEEN EXPERIMENTALLY DETERMINED AND CALCULATED VISCOSITIES, FROM DATA OF ARCHBUTT AND DEELEY

VISCOSITY AT 100° C.			VISCOSITY AT 15.6° C.		
BY TEST	Calculated from Viscosity at Lower Temperatures	Ratio	BY TEST	Calculated from Viscosity at Higher Temperatures	Ratio
0.046	0.041	1.12	0.42	0.59	0.71
0.070	0.067	1.04	1.008	1.10	0.92
0.080	0.080	1.00	1.118	1.12	1.00
0.033	0.030	1.10	0.453	0.67	0.68
0.039	0.033	1.18	0.727	1.09	0.67
0.049	0.041	1.20	1.138	1.79	0.64
0.058	0.050	1.16	1.915	2.85	0.67
0.063	0.058	1.09	2.172	2.66	0.82
0.076	0.073	1.04	3.046	3.48	0.88

It is not certain whether there is a definite temperature at which there is a change in the viscosity-temperature relation, or whether the apparent change is due to error in the form of equation. Hurst[18] expresses the opinion that "there is what may be called a 'critical point' at which temperature the oil begins to lose its viscosity more rapidly, and below which point the loss of viscosity on heating is very slow; this critical point varies with different oils, but the author has not been able to do more than make a few tentative experiments on the subject." As Hurst does not give even the approximate temperature at the critical point, it is not clear whether it occurs at very high temperatures and is due to disintegration, or at a moderate temperature and is due to some error in viscosimetry or to the presence of paraffin crystals at temperatures below the melting point of paraffin wax.

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[18] "Lubricating Oils, Fats, and Greases," **1911**, 243.

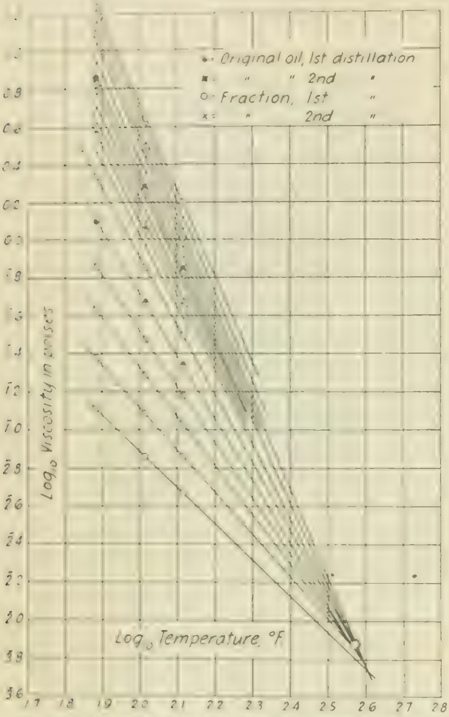

FIG. 9—FRACTIONS OF SINGLE SAMPLE OF NAPHTHENE BASE OIL

There is some evidence that Equation 7, with A equal to the solidification temperature, is more accurate and covers a wider range of oils than Equation 8. Ellis found that some of the more viscous oils did not give a straight logarithmic graph, but if the temperature above the point of complete solidification was used instead of temperature in °F., substantially straight lines were obtained even with these oils. Fig. 4 also shows fairly straight graphs for the most viscous oils. There is, however, some objection to the introduction of the solidification temperature into an equation, as the laboratory method for exactly determining this temperature is doubtful, and Equation 8, with temperatures in °F., has therefore been adopted, as sufficiently accurate for practical purposes for the majority of oils most frequently used, and as most convenient for graphical methods.

APPLICATIONS OF THE LOGARITHMIC VISCOSITY-TEMPERATURE DIAGRAM

PARAFFIN BASE OILS—All the American mineral oils tested by Archbutt and Deeley appear to have been of paraffin base, with the exception of the two oils of lowest viscosity, so that Fig. 5 may be taken as the diagram for paraffin base oils, which indicates the approximate intersection of the graphs for oils of this base. As will be seen later, there is a different point of intersection for each other class of oils, as observed by Dean and Lane but disregarded by Oelschläger.

NAPHTHENE BASE OILS—Fig. 6 shows tests[19] upon American oils of naphthene base, together with some foreign oils. Most of the graphs are fairly straight, the most marked exceptions being the fuel oils from Mexico and Persia.

The Mexican fuel oil showed marked viscosity hysteresis, and according to Dunstan and Thole[20] this phenomenon "is one eminently characteristic of colloids." Thus it would appear that the curvature of the graphs for fuel oils is probably due to the presence of colloids, a conclusion which has some support from the work of Seaton, Probeck and Sawyer,[21] who found, with varnishes, that the shape of the viscosity-temperature graph is determined by the amount of colloids.

Fig. 7, from data of Dunstan and Thole, does not show any marked relation between the amount of acid treatment and the form of graph, although colloids are removed by acid treatment. This may, however, merely prove that colloids were not present in large quantities in the oils as received by Dunstan and Thole, which is quite possible, since the phenomenon of viscosity hysteresis is comparatively rare.

The data concerning Russian and Scotch oils, Fig. 8, are not sufficient to locate points of intersection, for oils of moderate viscosity, as in Figs. 5 and 9. The only curved graph is for one of the Scotch oils; it has been found that oils of such low viscosity always show curved graphs.

Thus it may be concluded that the great majority of mineral oils of moderate viscosity will show approximately straight graphs, but there is more uncertainty in assuming a straight

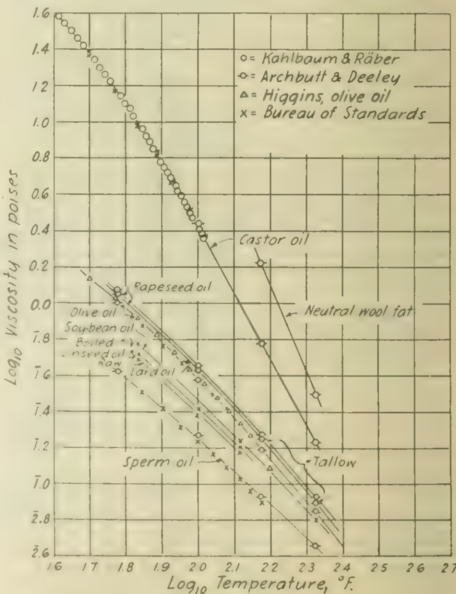

FIG. 10—ANIMAL AND VEGETABLE OILS

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[19] W. F. Parish, *J. Am. Soc. Naval Eng.*, **32** (1920), 45; W. F. Higgins, *Nat. Phys. Lab. Collected Researches*, **11** (1914), 10; **13** (1916), 281.

[20] *J. Inst. Petroleum Tech.*, **4** (1917–18), 201.

[21] THIS JOURNAL, **9** (1917), 35.

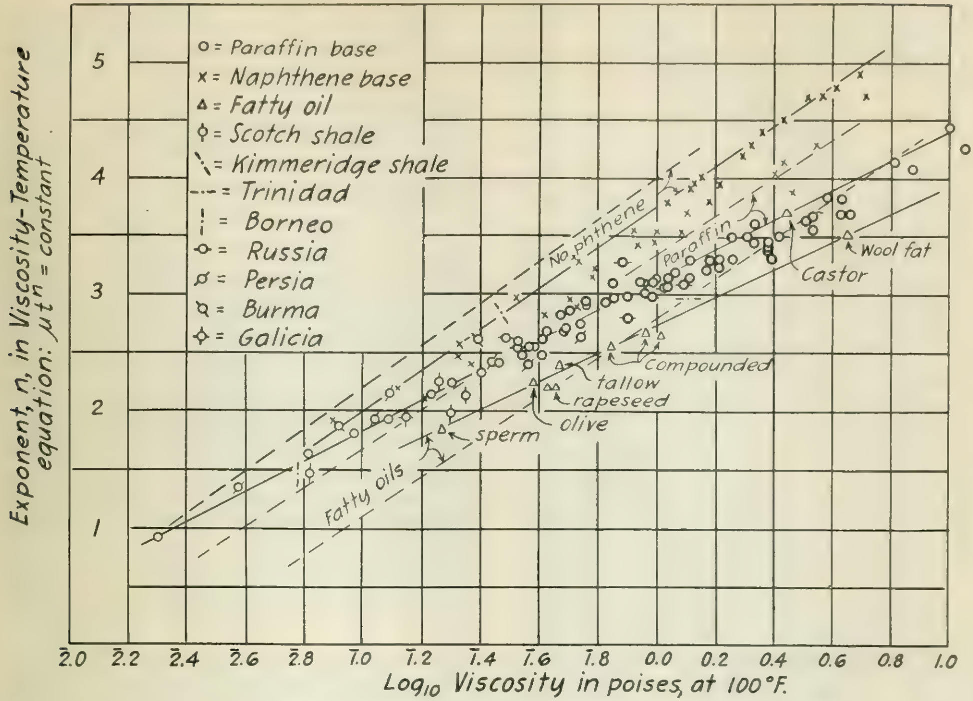

FIG. 11—DIAGRAMS TO FIND SLOPE OF LOGARITHMIC CURVES

graph for an unrefined than for a refined lubricating oil of the same viscosity. MacCoull[22] has devised a special cross-section paper which gives straight lines when Saybolt viscosity, in seconds, is plotted against temperature in ° F., but this diagram gives curved lines for the same oils which appear curved on the ordinary logarithmic diagram.

THE EFFECT OF NARROW CUTS—In order to determine whether the range of boiling point influences the shape or slope of the graph, a sample of naphthene base lubricating oil was subjected to a fractional distillation, without steam, at 1.5 mm. absolute pressure, so as to avoid cracking.[23] Of the resulting ten fractions, Fraction 8 was selected for a second distillation, after having been discolored with part of the residue from the first distillation. It was due to this contamination that the original oil of the second distillation had, as shown by Fig. 9, a slightly higher viscosity than Fraction 8 of the first distillation.

Fraction 5 of the first distillation has practically the same viscosities at all temperatures as the original oil. In the second distillation the same is true of Fraction 6, so that the evidence appears to be that narrowness of cut does not influence the slope of the logarithmic graphs; in other words, the value of n in Equation 8 depends upon the viscosity of the oil at a given temperature, but not upon the boiling point range.

It will be noted that all the oils on Fig. 9 are strictly from one crude, being in fact all fractions of the same sample, and it would therefore be expected that the point of intersection would be more clearly defined than in Fig. 5 where the oils were probably from different localities.

FATTY OILS—As already indicated by Fig. 4, the graphs of fatty oils are more curved, but not so steep on the average, as those for mineral oils. Fig. 10 also shows that with fatty oils, as with mineral oils, the curvature is most for the lighter oils at the lower temperatures. The graph for castor oil, from data of Kahlbaum and Räber[24] and others, and the two graphs for rapeseed oil, show that there is considerable error in the assumption that two samples of a given kind of fatty oil will have the same viscosity. Such oils cannot therefore be regarded as liquids of "known viscosity" for use in calibrating viscosimeters, unless the viscosity of the particular sample in question has been determined.[25]

METHOD OF CALCULATING POINT OF INTERSECTION OF LOGARITHMIC GRAPHS

DIAGRAM FOR DETERMINING THE VALUE OF n IN EQUATION $\mu = \frac{K}{t^n}$—It may be seen in Figs. 5 to 9 that the steepness of the slopes of the graphs increases with the viscosity of an oil at a given temperature. If as in Fig. 11, n, which is a measure of the slope, is plotted against the logarithm of the viscosity at a standard temperature, the data can be fairly well represented by three straight lines, for naphthene base, paraffin base, and fatty oils, respectively.

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[22] *Lubrication*, June **1921**, 5.

[23] It was found by J. E. Schulze, formerly of the Bureau of Standards, who developed this method, that if suitable precautions were taken to prevent leakage, the distillation could be carried to 300° C. (572° F.) without cracking.

[24] Quoted in *Bur. Stds., Technologic Paper* **112** (1919), 24.

[25] The Bingham viscometer (*Bur. Stds., Sci. Paper* **298**) was used for determining the viscosity of the fractions shown in Fig. 9. It is used to determine the viscosity of calibrating liquids, having a kinematic viscosity not over 0.5, but is not considered accurate for more viscous liquids on account of drainage error.

The greater scattering of the points for naphthene base oils is probably due to a large extent to the natural tendency to regard any oil, not of paraffin base, as a naphthene base oil. Thus oils from mid-continent crudes, or blends of paraffin with naphthene base oils, may have been classed and plotted with the naphthene base oils. However, the upper limit of points in Fig. 11, as determined by oils of Fig. 9, is clearly defined.

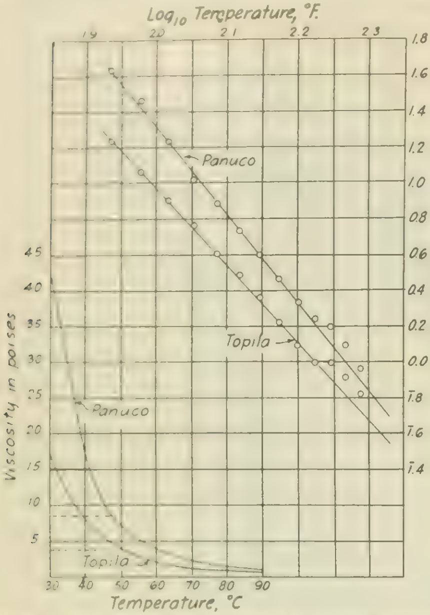


FIG. 12—VISCOSITY-TEMPERATURE GRAPHS FOR TWO MEXICAN CRUDE OILS

It will be noted that castor oil is an exception to other fatty oils, and that the commonly accepted belief that it "thins out less with the heat" than do paraffin base oils, is a delusion.

In order to get a definite value of n from the curved graphs of Fig. 10, it was necessary to assume straight lines between certain temperatures. These temperatures were taken, as for the mineral oils also, as 100° and 212° F. (37.8° and 100° C.). Since tallow and wool fat are solid at the lower temperature, it was necessary to find the slope from a shorter range of temperature.

The oils marked "compounded" were mineral oils containing a blown fatty oil, which indicates a convenient way to decrease the temperature coefficient of viscosity. Blown oils, however, increase in viscosity with time.

Fig. 11 gives all the data necessary for finding the constants in Equation 8 if the viscosity has been determined at the standard temperature of 100° F. (37.8° C.). Then

[illegible] (12)

where μ_1 is the viscosity at 100° F., in poises. Entering Fig. 11 with log μ_1 the ordinate n may be read, and K calculated from Equation 12. Then for any other temperature

[illegible] (13)

which is about equal in simplicity to Equation 10.

EQUATIONS CONNECTING THE n DIAGRAM WITH THE LOGARITHMIC VISCOSITY-TEMPERATURE DIAGRAM—A straight line on Fig. 11 may be represented by an equation of the form

$$n = \mathrm{H}\ (\log \mu_1 + \mathrm{E}) \qquad (14)$$

where H is the tangent of slope and E is the value of $-\log \mu_1$ where the line intersects the axis of abscissas. By a modification of Oelschläger's method, using absolute viscosity at 100° F. (37.8° C.) instead of the viscosity factor at 20° C. (68° F.), and assuming that logarithmic graphs meet at a point,

$$\frac{\log \mu - \log \mu_0}{\log \mu_1 - \log \mu_0} = \frac{\log t_0 - \log t}{\log t_0 - \log 100} \qquad (15)$$

where t_0 and μ_0 are the coördinates of the point of intersection of the logarithmic graphs for oils of the crude under consideration, and μ is the viscosity at any temperature, t.

It should of course be kept in mind that there is no certainty that logarithmic graphs should be straight above 100° C. (212° F.), so that t_0 should be regarded as a means of calculation rather than as the temperature at which all oils of a certain class would actually have the same viscosity. There is some evidence, however, that the viscosity-temperature relation follows the same law for a considerable range above the boiling point of water, as below it, for Dean and Lane made two tests at 180° C. (356° F.) and found close agreement between the observed and extrapolated viscosities.

By combining Equations 14 and 15,

$$\mathrm{H} = \frac{1}{(\log t_0) - 2} \qquad (16)$$

and

$$\mathrm{E} = -\log \mu_0 \qquad (17)$$

by means of which a point of intersection may be calculated on Figs. 5, 9, and 10, corresponding to the full lines on Fig. 11. The calculated as well as the graphically determined points are given in Table III, the calculated points being shown on Figs. 5 and 9 by double circles.

TABLE III—COÖRDINATES OF POINTS OF INTERSECTION OF LOGARITHMIC GRAPHS

CLASS OF OILS	log μ_0	μ_0	log t_0	t_0
Paraffin base, Fig. 5..........	$\bar{2}$.00	0.010	2.60	398
Naphthene base, Fig. 9.......	$\bar{3}$.78	0.006	2.59	389
Fatty oils, Fig. 10............	$\bar{2}$.35	0.022	2.56	363
Paraffin base, calculated......	$\bar{3}$.58	0.0038	2.77	589
Naphthene base, calculated...	$\bar{3}$.88	0.0076	2.57	371
Fatty oils, calculated.........	$\bar{3}$.75	0.0056	2.82	661

Conversely, a line on Fig. 11 may be found corresponding to a certain point of intersection obtained graphically. The values of H and E are given in Table IV, both as obtained graphically and by calculation.

TABLE IV—DATA FOR LOCATING GRAPHS ON THE n DIAGRAM

	OBTAINED GRAPHICALLY			CALCULATED		
CLASS OF OILS	Intersection with Axis of Abscissas	E	Tangent of Slope	Intersection with Axis of Abscissas	E	Tangent of Slope
Paraffin base	$\bar{3}$.58	2.42	1.30	$\bar{2}$.00	2.00	1.67
Naphthene base	$\bar{3}$.88	2.12	1.75	$\bar{3}$.78	2.22	1.70
Fatty oils	$\bar{3}$.75	2.25	1.22	$\bar{2}$.35	1.65	1.79

The dotted lines on Fig. 11 were located by the calculated values in Table IV. It will be seen that these lines do not agree at all well with the experimentally determined graphs, shown in full lines. On the other hand, the calculated points of intersection, on Figs. 5 and 9, agree with the graphs as well or better than the points obtained graphically, so that it is preferable to calculate the point of intersection.

Before considering the temperature of average viscosity (which is a related but distinct subject) it may be well to summarize the practical applications of the method developed for estimating viscosities. It should be remembered that the change of viscosity with the temperature does not follow any known theoretical laws (except in the case of certain liquids of definite chemical composition) and that mathematically exact calculations cannot be made. Thus a simple method of estimation or interpolation is of value, even though the results may not be very accurate. An examination of empirical formulas leads to the adoption of the following method.

1—Using oils all from the class or crude under consideration, make a logarithmic diagram, A (similar to Fig. 9), where absolute viscosity is plotted against the temperature in ° F.

2—With data from Diagram A, discarding curved graphs, and using only those which, when prolonged, would approximately meet at a point, construct a second diagram, B (similar to Fig. 11), where, for each oil, the slope of the logarithmic graph is plotted against the logarithm of the absolute viscosity at 100° F. Average the points on Diagram B by a straight line, and find the slope and the point of intersection of this line with the axis of abscissas.

3—Calculate, by Equations 16 and 17, the point of intersection of the logarithmic graphs on Diagram A. This diagram can then be used to estimate change of viscosity with the temperature, for oils of medium viscosity, of the crude in question. A new diagram would have to be made only when a new crude was considered.

4—To estimate the viscosity of an oil at, say, 122° F. (50° C.), locate the point on Diagram A (for the crude in question) with abscissa equal to 2.000, the logarithm of the standard temperature of 100° F., and with ordinate equal to the logarithm of the absolute viscosity at that temperature. This point, together with the point of intersection of the logarithmic graphs, previously located, determines the graph of the particular oil in question.

5—As the logarithm of 122 is 2.086, the logarithm of the desired absolute viscosity at 122° F. may be read from the graph just determined, at the point where the abscissa has that value.

THE TEMPERATURE OF AVERAGE VISCOSITY

In pumping through pipes, the oil is given an initial temperature, t_1, in order that it may not be too viscous when the final temperature, t_2, is reached. In order to estimate the loss of pressure, the temperature of average viscosity, t_a, must be calculated, for which Mancero[26] gives the equation, due to the Standard Oil Company of California:

$$t_a = {}^2/_3\, t_1 + {}^1/_3\, t_2 \tag{18}$$

which is equivalent to

$$t_a = t_1 - \frac{t_1 - t_2}{3} \tag{19}$$

and may be used with either the Fahrenheit or Centigrade scale.

If it is assumed that Equation 8 is correct, it may be shown that [27]

$$t_a = \sqrt[n]{\frac{(1 - n)\ (t_1 - t_2)}{t_6^{1-n} - t_2^{1-n}}} \tag{20}$$

Mancero gives two curves, for Panuco and Topila oils, "prepared by La Carona Oil Co.," with absolute viscosity plotted against temperature in °C., from 30° to 90° C. (86° to 194° F.). Both curves show a point of reverse curve at about 75° C. (167° F.), which is not so plainly visible in the lower part of Fig. 12, reproduced from Mancero's data. The upper part of Fig. 12 shows logarithmic graphs of these same oils, which are straight except at the highest temperatures. The irregularity at high temperatures is probably due to some inaccuracy in viscosimetry.

The temperature of average viscosity was obtained from Fig. 12 by planimeter and by Equation 20 in ° F., with $n = 4.26$ for the Topila oil having an absolute viscosity of 0.96 at 100° F. (37.8° C.) and with $n = 4.88$ for the Panuco oil, with viscosity of 1.30 at the same temperature. The results are given in Table V.

TABLE V TEMPERATURE OF AVERAGE VISCOSITY OF TWO MEXICAN OILS

	By Planimeter			By Equation			
				19		20	
	Average Viscosity	Temperature of Average Viscosity		Temperature of Average Viscosity		Temperature of Average Viscosity	
OIL	Poises	° F.	° C.	° F.	° C.	° F.	° C.
Topila....	3.8	122.9	50.5	122	50	121.1	49.5
Panuco...	8.5	118.4	48.0	122	50	120.5	49.2

Thus for the particular oils and range of temperature in question, there is little choice in regard to accuracy between Equations 19 and 20, either of which is accurate enough for practical purposes, and far more accurate than any method of estimating the temperature of the ground, and the consequent value of t_2. While Equation 20 might prove to be of more general application, Equation 19 is far simpler to use in calculations.

[26] Juan Mancero, *Oil Weekly*, **17** (1920), 84; translated from the Spanish by John F. Dodge.

[27] The writer is indebted to Dr. H. L. Dryden of the Bureau of Standards for Equation 20.

Notes on Determination of Absolute Viscosity of Petroleum Oils[1]

By W. H. Fulweiler and C. W. Jordan

UNITED GAS IMPROVEMENT CO., 319 ARCH ST., PHILADELPHIA, PA.

The absolute viscosity of a number of samples of petroleum, animal, and vegetable oils has been examined. All of these samples showed changes in viscosity when the material was allowed to stand in glass viscosimeters for 24 hrs. With two samples that were retested after standing for a number of weeks, the sign and magnitude of the change was practically the same as that observed after 24 hrs.' standing in the viscosimeter. Apparently, samples of oil intended as viscosity standards should be checked from time to time until more is known regarding the nature and extent of the change on standing.

THE authors have recently had occasion to make a careful determination of the absolute viscosity of several samples of petroleum oil and have found that in some cases there is considerable change in viscosity on standing. It was further noticed that the viscosities showed marked changes when the oil was allowed to remain in the glass viscosimeter for periods of from 24 to 72 hrs., these changes being of the order of 0.5 per cent when the precision of the observations was of the order of 0.1 per cent. These results may be of interest, especially in connection with the use of samples of oil as viscosity standards over long periods.

APPARATUS

The apparatus was of the Bingham and Green type. Two viscosimeters were used on each sample. In the No. 1 instrument the capillary was 24 cm. in length and approximately 0.416 mm. in diameter,[2] in the No. 2 instrument the capillary was 10 cm. in length and approximately 0.918 mm. in diameter.[2]

The thermostat had a capacity of 60 gal. The circulation was obtained by means of an external pump, and the temperature control was such that temperatures constant to within ±0.005° were readily maintained. The thermometer had

[1] Presented before the Section of Petroleum Chemistry at the 63rd Meeting of the American Chemical Society, Birmingham, Ala., April 3 to 7, 1922.

[2] Calculated from the "C" constant of the instruments.

recently been standardized by the Bureau of Standards and was read with a microscope.

Considerable attention was given to the method of reading the pressure. Owing to the fact that the capillary of the No. 1 viscosimeter was quite small, it was necessary to use pressures as high as 85 cm. of mercury in order to obtain a reasonable time of flow. It was, therefore, decided to use a mercury manometer and to read this with a cathetometer. It was believed possible to secure in this manner quite as high a degree of accuracy as would have been secured had the ordinary water manometer with the steel tape been used.

When the time of flow exceeded an hour, the writers found considerable difficulty in securing an accurate record of the time. Although the ordinary stop watch may be of sufficient accuracy where the time does not exceed 5 min., it appears to show large errors when times of an hour or more have to be measured. The ordinary stop watch is quite difficult to regulate and even more difficult to keep in adjustment, but the writers finally found a watch that could be checked within one second in an hour against an astronomical clock. It would appear that there is quite a field of usefulness for a piece of apparatus, not too expensive, which would give accurate time intervals up to an hour.

In connection with the standardization of the apparatus, the writers found the great need, which has been spoken of by other observers, for a pure and reproducible material that would have a viscosity at ordinary temperatures of 40 to 50 centipoises.

The No. 1 viscosimeter was standardized with water and 50 per cent ethyl alcohol. The No. 2 viscosimeter was standardized with 50 per cent ethyl alcohol, 40 per cent sucrose, and 60 per cent sucrose. Bureau of Standards sucrose was used in making up the sucrose solutions.

RESULTS

A very highly refined white medicinal oil gave an absolute viscosity at 37.78° C. of 40.36 centipoises. When this material was allowed to stand in the viscosimeter for 24 hrs., the viscosity decreased by 0.54 per cent. On retesting this sample 2 mo. later, the viscosity had decreased by 0.43 per cent.

A petroleum oil of reddish color which had been refined by filtration gave a viscosity of 38.35 centipoises. On standing 24 hrs. in the viscosimeter the viscosity increased by 0.42 per cent. This sample after standing 5 wks. in a tin can had increased by 0.42 per cent.

The greatest number of observations were made on this sample. They showed a gradual increase in viscosity with time, the observed figures being for the fresh sample as given above, 38.35, then 38.36, 38.41, and the last observation 5 wks. later, 38.46.

In order to get some further information regarding the possible sign and extent of this change on standing, two samples of petroleum oil furnished by Dr. Delbridge of the Atlantic Refining Company were examined. It is understood that one of these oils was refined by filtration, while the other was not. Samples of both were exposed on the roof in white glass bottles for a week. The filtered oil showed no change in the viscosity between the sample exposed to the light and the sample kept in the dark, while the unfiltered oil showed an increase of 1 per cent in the sample that had been exposed to the light.

A sample of castor oil showed an increase of 0.33 per cent on standing in the viscosimeter for 24 hrs., while a sample of lard oil showed a decrease of 0.3 per cent on standing in the viscosimeter for 24 hrs.

The writers have not as yet formulated any theory of the cause of these changes; it may be pointed out, however, that the fact that the results were checked with viscosimeters of both wide and narrow bore apparently excludes the formation of films of material dimensions on the inside surface of the capillary, thus changing the bore. It may be, however, that an adsorbed film of molecular dimensions is formed in the capillary and that this adsorbed film has a different viscosity from that of the oil.

It is the intention of the writers to retest some of these samples for a number of months in order to determine, if possible, whether they will come into equilibrium or whether the change will be continuous. This study should be of some importance as affecting the usefulness of samples that are to be retained for long periods as standards of viscosity.

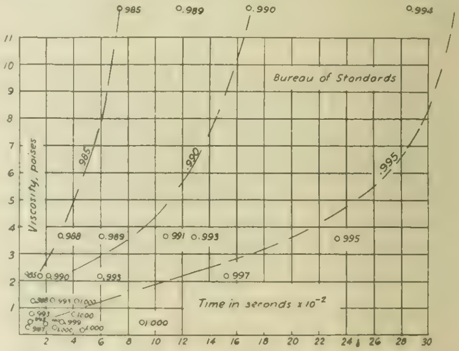
The Drainage Error in the Bingham Viscosimeter

By Winslow H. Herschel

BUREAU OF STANDARDS, WASHINGTON, D. C.

[Discussion of preceding paper]

It is well known that the volume discharged from a flask is less than the volume it will receive, even when the calibration is made with water, and this is even more the case when a more viscous liquid is used. It follows that the discharge with oil is less than the discharge with water.



The Bingham viscosimeter is so arranged that the bulb becomes wet in fixing the working volume, so that it is difficult to observe or measure the drainage error. Comparisons of various viscometers led to the conclusion that the error was serious enough to require investigation, and a special instrument was made up with a bulb similar in shape and size to that of the Bingham instrument, and so arranged that the drainage error could be measured by calibration with liquids of various viscosities. On the diagram, which shows the results to date, the numbers on points give correction factors by which the constant C of the Bingham viscosimeter, obtained by calibration with water, must be divided to obtain the value to be used in obtaining the viscosity of liquids having a higher viscosity than that of the calibrating liquid. The diagram may also be used to determine the time of flow necessary to render the drainage error negligible.

In the Annual Report of the American Metric Association recently issued, engineers, business men, and manufacturers who favor the adoption of the metric system in the United States are quoted at length, and the story of the extension of its use during 1921 is told. The use of the metric system is now obligatory in 46 countries.

Sulfur Compounds and Oxidation of Petroleum Oils[1,2]

By C. E. Waters[3]

Department of Commerce, Bureau of Standards, Washington, D. C.

In general, mineral lubricating oils which contain large percentages of sulfur compounds are more easily oxidized than those in which there is less sulfur. This is true whether the oils are heated to 250° C. or exposed to sunlight.

The residues left behind on cracking and partly distilling off oils, as in the Conradson carbon residue test, tend to retain the sulfur in the oil.

The bearing of these facts upon the formation of sludge in transformer and turbine oils, and of carbon in internal combustion engines is pointed out in the following paper.

In earlier work on the oxidation of mineral lubricating oils,[4] it was found that, contrary to expectation, the addition of free sulfur to an oil caused no great difference in the amount of asphaltic matter formed by heating it in the air. In other words, the presence of sulfur did not appreciably affect the rate of oxidation of the oil.

This result was not only unexpected, but it was contrary to what others have found when oil is heated in contact with sulfur and sulfur dioxide.[5] If there is any explanation other than experimental errors, it is that the amount of sulfur added, 0.10 per cent, was too small to affect appreciably the rate of oxidation of the oil. Data accumulated during the past two years seem to uphold this explanation in general.

Carbonization Value of Oils

In a "carbonization" test for motor oils developed by the author, the oil is heated to 250° C. in contact with air, for 2.5 hrs., diluted with petroleum ether, and the precipitate is filtered off and weighed. The result, calculated as percentage of the weight of original oil, is called the "carbonization value." From time to time the carbonization values and sulfur content of motor oils are determined, simply to accumulate data on the possible relation between the two. In nearly every case it has been found that oils which contain much sulfur in combination almost always have comparatively high carbonization values. In general, low sulfur and low carbonization go together, but not always, because other things than sulfur compounds can increase the rate of oxidation of the oil.[6]

The data on thirty-seven oils, all that have been examined, can be summarized in Table I.

Table I—Relation of Sulfur Content to Carbonization Value

Number of Oils	Carbonization Value Per cent	Sulfur Per cent
8	Trace–0.10	0.04–0.08 (One with 0.21)
6	0.11–0.30	0.18–0.29 (One each with 0.05 and 0.90)
14	0.31–0.75	0.17–0.63 (Two with 0.82)
4	0.76–1.25	0.17–0.61
5	1.26–4.55	0.37–0.46

There are irregularities in the table, and the data are too few to be the basis of any well-founded generalization, but there seems to be a tendency toward high carbonization with high sulfur. The matter is complicated by the presence in the oils of substances other than sulfur which can cause accelerated oxidation, as in the case of the oil which contained but 0.05 per cent of sulfur but had a carbonization value of 0.29. Four other oils with relatively high sulfur had carbonization values which were unexpectedly low. These results can be accounted for on the supposition that the sulfur compounds resisted oxidation.[7] This is not an improbable assumption.

It is not the intention of this paper to formulate a general indictment against oils which contain more than a few hundredths of a per cent of sulfur, because there is not enough experimental and practical evidence to justify such a course. However, it does not seem unfair to say that such oils, except those used for cutting, are not above suspicion. No chemist, if forced to choose between two oils identical in every respect except their sulfur content, would select the one with the greatest percentage of that element as being the one least likely to deteriorate when used under oxidizing conditions. If he did make such a selection, how would he justify it?

Effect of Heat on Sulfur Compounds in Oils

Granting for the sake of discussion that sulfur compounds are contributory causes to rapid oxidation, what happens to these compounds when oil containing them is heated in the air? Part is lost either by direct evaporation or after cracking, and hydrogen sulfide and oxides of sulfur are to be looked for in the escaping gases and vapors. A considerable part of the sulfur is to be found in the asphaltic matter which is thrown down by the addition of petroleum ether to the oxidized oil. The oil filtered off from the precipitate contains less sulfur than it did before heating.

A 6-g. sample of California cylinder stock, which contained 0.80 per cent of sulfur, was heated in an all-glass apparatus so constructed that a slow current of air could be passed into the oil and out through a flask partly filled with a solution of sodium hypobromite. The oil was kept at 240° to 260° C. for 3 hrs. Only a film of oily distillate passed over. When the hypobromite was acidified, the addition of barium chloride immediately produced a dense precipitate of barium sulfate. Drops of moisture on the inside of the tube leading into the flask were strongly acid to congo red paper, which does not change color with weak acids. This oil gave off hydrogen sulfide when heated in a test tube to 250°, and perhaps the drops were formed by oxidation of this gas.

The following experiments show that only part of the sulfur is lost when oils are heated in air, and that this element takes part in the formation of the asphaltic matter thrown down by the addition of petroleum ether. Three oils were used: C, the California cylinder stock just discussed; O, a commercial lubricant of unusually high carbonization value; and M, a motor oil to which topped Mexican crude had been added to increase its sulfur content. Ten-gram samples were heated to 250° C. for 2.5 hrs. in open flasks. When cold, the flasks were weighed to determine the loss by evaporation. The residual oil was then diluted with 50 cc. of petroleum ether,

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[1] Received March 27, 1922.

[2] Published by permission of the Director of the Bureau of Standards.

[3] Chemist, Bureau of Standards.

[4] *Bur. Stds., Technologic Paper* **4** (1911), 9 and 11; This Journal, **3** (1911), 814.

[5] Holde and Eickmann, *Mitt. kgl. Materialprüfungsamt*, **1907**, 145; *Z. angew. Chem.*, **20** (1907), 1263, 1923; Southcombe, *J. Soc. Chem. Ind.*, **30** (1911), 261.

[6] *Bur. Stds., Technologic Paper* **177** (1920), 8; *Circ.* **99** (1920), 13.

[7] The definite statement that oils may contain sulfur so well "protected" that it resists oxidation was recently made to the author by a chemist employed at one of the large eastern refineries.

and the flasks were corked. Next day the precipitates were filtered off in Gooch crucibles, washed with petroleum ether, dried at 105° C., weighed, and analyzed for sulfur.

The oily filtrates were freed as completely as possible from the ether by warming first on the steam bath and then in an oven at 105°. It is believed that the error resulting from this procedure was not unduly large.

Table II [illegible] Data on Three Oils

Oil	C	O	M
[illegible], per cent	0.10	4.55	1.91
[illegible], per cent	0.80	0.46	0.39
[illegible], per cent	3.37	22.06	15.54
Sulfur in asphaltic precipitate, per cent	1.05	2.03	4.88
Sulfur in oil filtered off, per cent	0.72	0.35	0.26
Total Sulfur Accounted for			
In asphaltic precipitate, gram	0.0001	0.0112	0.0093
In oil filtered off, gram	0.0695	0.0253	0.0215
Sulfur found, gram	0.0696	0.0365	0.0308
Sulfur in unheated oil, gram	0.080	0.046	0.039
Sulfur lost, gram	0.0104	0.0095	0.0082
Percentage of sulfur lost	13.00	20.65	21.03

It is plain from the figures in Table II that there is a tendency for the sulfur to accumulate in the asphaltic matter which is formed by oxidation and polymerization. Some is also to be found in the highly oxidized varnish-like coating on the walls of the flasks. With these three oils the amount of this varnish was less than 3 mg., so that a quantitative determination of sulfur was out of the question, although qualitative tests were obtained.

Table III Sulfur in Distillation Residues

(All figures are expressed as percentages)

Oil	C	C	P	P	N	N	S	S	S[1]	W	W	W
Sulfur in oil	0.80	0.80	0.18	0.18	0.19	0.19	0.44	0.44	0.44	0.79	0.79	0.79
Residue	25.2	17.2	19.4	34.2	46.0	16.2	13.6	22.2	10.0	17.4	23.3	3.4
Sulfur in residue	0.78	0.80	0.24	0.20	0.20	0.26	0.99	0.77	1.24	2.49	2.12	7.24
Sulfur retained	24.4	17.2	25.6	37.7	48.4	22.1	30.5	38.6	28.1	54.9	62.8	31.1

[1] Only 4.20 g. of oil were left for this test.

If the data given above are not in conflict with the behavior of oils in actual use, the deposits formed from turbine and transformer oils should contain sulfur. A typical steam turbine sludge analyzed by Mr. Anderson of this Bureau was found to contain 0.33 per cent of sulfur, or 0.65 per cent, calculated on the oil-free basis. Similarly, the oil-free deposit in a transformer contained, according to an analysis by Mr. Berryman, 0.57 per cent of sulfur.

Carbon from Internal Combustion Engines

A few samples of "carbon" taken from internal combustion engines have also been analyzed. In twelve analyses, the percentages of sulfur found in the oil-free material were from 0.52 to 3.08. The amounts of ash, 2.87 to 11.87 per cent, varied independently of the sulfur. The benzene-soluble portions of three carbon deposits contained 0.94, 1.33, and 1.52 per cent of sulfur, respectively.

In order to learn something more about the accumulation of sulfur in the "carbon" deposits formed in internal combustion engines, a few oils were subjected to the following treatment: 5-g. samples were heated in 100-cc. porcelain crucibles which rested on a wire triangle at the bottom of a larger iron crucible. The porcelain crucibles were covered with watch glasses, so that the heating could be stopped when only a small part of the oil was left.

This form of apparatus was used in preference to the Conradson carbon residue apparatus because it was easier to stop the distillation at any desired point short of dryness. It might be objected that the simpler apparatus would not give results comparable with those obtained with Conradson's. [illegible] objection. In the first place, the object was to learn something of the fate of the sulfur during destructive distillation of the oil, and almost any apparatus from which air was reasonably well excluded would serve the purpose. No form of apparatus can duplicate the conditions in an engine.

In the second place there was no need of driving off all but the residue of coke, for then no sulfur would be left unless strongly basic metals were present. Besides, no one claims that the deposits in an engine are really carbon. Apart from soot, dust, and similar extraneous matter, they consist largely of the last portions of the destructive distillation of the oil and fuel, or oxidation products, or both.[8]

When only a small part of the oil was left, the heating was stopped. After cooling, the crucibles were cleaned as well as possible on the outside, and weighed. The sulfur in the residues was then determined in order to ascertain whether it tended to remain behind or to be driven off with the oil vapors.

The following oils were employed: C, the California cylinder stock already discussed; P, a paraffin base motor oil; N, a naphthene base motor oil; S, a heavy red oil containing "sulfonic acids;"[9] and W, a white medicinal oil from California mixed with topped Tampico crude.

In the case of every oil except C, the distillation residue contained a somewhat higher percentage of sulfur than the unheated oil. This is shown most clearly by S and W. The percentage of distillation residue, except for C, was less than the percentage of the original sulfur retained by the residue. This shows that the sulfur is not driven off as fast as the oil during the cracking and distillation. It is also significant that the smaller the amount of the distillation residue for a given oil, the greater the percentage of sulfur it contains. This is most evident with S and W. In the last experiment with W, the residue weighed only 0.17 g., yet it yielded almost 0.090 g. of barium sulfate. It consisted of loose flakes of carbon and a varnish-like coating on the walls of the crucible.

Because the residue of carbon cannot possibly carry more than traces of sulfur, it follows that at the very end of the distillation there must be a rapid change in the sulfur content. It is difficult to check this by analysis, because the distillation cannot be stopped at the desired point, even though its progress can be watched. Besides, not enough sulfur for a satisfactory determination would be left. A simple distillation test was therefore made. About 5 cc. of oil, containing 0.88 per cent of sulfur, were distilled from a retort made by drawing out the open end of a hard glass test tube. Throughout the distillation the evolution of moderate amounts of hydrogen sulfide could be detected by means of lead acetate paper. At the end, when it became necessary to heat part of the retort to dull redness, hydrogen sulfide came off more freely than before.

The conclusion must be drawn that the presence of even considerable percentages of sulfur in a "carbon" deposit in an internal combustion engine is not evidence in favor of either the oxidation test or the carbon residue test.

Finally, in order to ascertain whether the presence of sulfur compounds caused rapid oxidation at ordinary temperatures, a series of experiments was made by exposing oils to the action of sunlight and air for 100 hrs. Ten-gram samples were

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[8] *Bur. Stds., Circ.* **99**, 39. Published statements bearing on this point are there discussed.

[9] Distributed in **1920** by F. R. Baxter for cooperative work on sulfur by Committee D-2, American Society for Testing Materials.

TABLE IV—OXIDATION OF SULFUR COMPOUNDS IN SUNLIGHT

(Values expressed in per cent)

SAMPLE	4	5	C	W Oxidized	W Not Oxidized
Sulfur in original oil	0.23	0.70	0.80	0.79	0.79
Change in weight in sunlight	+1.04	+0.66	+0.66	−0.87	...
Precipitate	0.57	0.29	0.11	3.71	3.08
Sulfur in precipitate	1.24	6.49	9.52	7.82	7.98

exposed in 150-cc. Erlenmeyer flasks from which dust was excluded by filter papers folded over their mouths. After exposure, 50 cc. of petroleum ether were added to each flask, which was then corked. Next day the precipitates were filtered off in Gooch crucibles, washed with the ether, dried at 105° C., and weighed. They were then analyzed for sulfur. The results are given in Table IV.

Of these four oils, W was the only one which gave a precipitate when diluted with petroleum ether before oxidation, and only this oil lost in weight during the 100-hr. exposure. The latter fact may or may not be related to the lower sulfur content of the precipitate from the oxidized oil.

The precipitates all contained surprisingly large percentages of sulfur, and there can be no reasonable doubt that compounds of this element play an important part in the oxidation of the oil in sunlight. There are indications of the formation of sulfuric acid or its esters.

Comparison of Wood Cellulose and Cotton Cellulose[1]

By S. A. Mahood[2] and D. E. Cable[3]

FOREST PRODUCTS LABORATORY, MADISON, WISCONSIN

Data recorded in this paper show that the wood cellulose most nearly corresponding to cotton, taking purified linters as a standard, is obtained by recooking "easy bleaching" sulfite pulp with soda and bleaching with 2 per cent bleach. The significant differences are found in the amounts of furfural-yielding constituents present and in the γ-cellulose contained in this pulp but which is not found in the linters. This sample, however, represents the lowest yield on the basis of the original wood.

The recooked, raw cooked sulfite pulp (232 LR) bleached with 3 per cent bleach does not differ so markedly from the above sample and represents a 6 per cent higher yield on the basis of the original wood. Esterification tests might show this to be a suitable form of raw material, assuming that similarity to cotton cellulose is a prerequisite for wood cellulose for this purpose.

Since the data show that bleaching is a very efficient method of removing the noncellulose material it is probable that the yield of cellulose suitable for the manufacture of esters could be materially increased by giving a light or raw cooked stock a bleaching treatment prior to recooking with soda.

Alkaline cooking produces a larger amount of β-cellulose than acid cooking, the amount increasing with the severity of the cooking conditions. From a chemical standpoint, pulps produced by alkali are less similar to cotton than those produced by acid cooking or by acid and alkaline cooking. On this basis the former appears to be less suitable for esterification.

On the basis of the data given, cellulose from wood and cellulose from cotton do not represent identical chemical aggregates, and the same is true of wood celluloses obtained by acid cooking and by alkaline cooking. The practice of checking wood cellulose according to the specifications for cotton is therefore a questionable procedure.

IT is customary in determining the suitability of wood cellulose, to be employed as a substitute for cotton cellulose in the manufacture of cellulose esters, to refer the former to specifications ordinarily applied to cotton. This practice is perhaps due more to lack of data regarding the celluloses than to lack of appreciation of the possible differences in the nature of these chemical aggregates. It is, of course, possible to obtain from wood by suitable means of degradation a cellulose that approximates cotton cellulose, but available information indicates that cellulose from wood cannot be made identical with cellulose from cotton. To obtain a product that even approximates cotton cellulose entails a loss so great that the process becomes uneconomical.

In connection with a study of the preparation of wood cellulose suitable for the manufacture of cellulose esters, comparisons were made of wood and cotton celluloses varying in purity from the original raw materials to severely cooked and highly bleached samples, for the purpose of (1) following the chemical changes which occur in wood pulps on successive cooking and bleaching treatments in order to determine whether the conditions in these treatments could be changed so as to increase the yield of suitably purified cellulose, and (2) determining so far as possible the points of similarity or difference of cellulose from wood and that from cotton. Data of this nature should be of value not only in the manufacture of cellulose esters, but also in all allied industries involving the chemical utilization of cellulose and also in the pulp and paper industry.

EXPERIMENTAL METHOD[4]

Since even "normal" or cotton cellulose is still an uncertain chemical entity, the method of attack in making these comparisons consisted in determining the constants usually stipulated in specifications for cotton[5] and also certain constants which have been employed in the analysis of the lignocellulose.[6]

Moisture was determined by drying at 105° C.; waxes, fats, and resins were found by extraction with ether for 4 to 5 hrs.; solubilities in 1 per cent alkali and in hot and cold water were obtained by treatment with those reagents for 1, 3, and 48 hrs., respectively. Pentosans and methylpentosans were determined by distilling the material under investigation with 12 per cent hydrochloric acid (sp. gr. 1.06), treating the furfural contained in the distillate with phloroglucinol, weighing the resulting mixed phloroglucides, and weighing again after the extraction of methylfurfural phloro-

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[1] Presented at the Cellulose Symposium of the Division of Industrial and Engineering Chemistry at the 60th Meeting of the American Chemical Society, Chicago, Ill., September 6 to 10, 1920.

[2] Chemist in Forest Products, Forest Products Laboratory, Madison, Wis.

[3] Assistant Chemist in Forest Products, Forest Products Laboratory, Madison, Wis.

[4] Acknowledgment is made to Messrs. M. W. Bray and J. A. Staidl for assistance in securing the data given in this paper.

[5] Weaver, "Military Explosives," **1912**, 188; Marshall, "Explosives," **1917**, 696; *Paper*, **23** (1919), No. 23.

[6] THIS JOURNAL, **9** (1917), 556; Cross and Bevan, "Paper-making," **1916**, 93.

TABLE I—YIELDS OF PULP

(Results expressed in per cents, based on oven-dry weight of wood)

[illegible]	[illegible]	[illegible] of Cook	Yields Unbleached Pulps	YIELDS—BLEACHED PULPS Bleaching Powder	Yield	Bleaching Powder	Yield	Bleaching Powder	Yield	Bleaching Powder	Yield	Bleaching Powder	Yield
[illegible] L	[illegible]	Sulfite	61.3	..	..	..	..	..	..	25	57.3	50	53.6
[illegible] L R	[illegible]	Recook	39.4	3.0	39.2	..	..	5	38.8	8	38.7	12	39.2
[illegible] W	[illegible]	Sulfite	47.3	2.5	47.9	6	45.6	12	46.2	20	45.5	30	46.4
[illegible] W R	[illegible]	Recook	33.3	2	32.7	..	..	5	32.4	7	32.3	12	32.0
[illegible] W	[illegible]	Soda	33.8	..	..	7	32.8	10	31.8	15	32.5	..	..
201 L	[illegible]	Soda	42.8	..	..	12	41.9	..	..	20	40.7	..	..
[illegible] W	[illegible]	Sulfate	39.0	..	..	6	38.7	15	39.2	..	..	..	..
[illegible] L	[illegible]	Sulfate	48.2	..	..	10	47.6	..	..	25	46.2	..	..

glucide by means of alcohol. Cellulose determinations were made by a modification of the method of Cross and Bevan, involving alternate treatment with chlorine gas and a 2 per cent solution of sodium sulfite to a point where no color resulted with the sulfite solution after treatment with chlorine. Acetic acid by hydrolysis was found by boiling for 3 hrs. with 2.5 per cent sulfuric acid, distilling the acid extract under a pressure of 40 to 50 mm., and titrating the resulting distillate with standard alkali. Methoxy groups were determined by distilling with hydriodic acid according to the Zeisel method.

Lignin, or the noncellulose content, was obtained by a modification of the method of Ost and Wilkening[7] employed in the hydrolysis of cellulose. Four grams of the pulp were extracted with ether and treated with ten times their weight of 72 per cent sulfuric acid, and hydrolysis was allowed to proceed for 16 hrs. at room temperature. The solution was then diluted to 3 per cent and boiled under a reflux condenser for 2 hrs. This caused a coagulation of the suspended material and the residue was then filtered on an alundum crucible, dried, and weighed.

Solubility in 7.14 per cent sodium hydroxide (or 10 per cent potassium hydroxide), which is regarded as a measure of the degree of bleaching, was determined by treatment of 2 g. of oven-dry pulp with 100 cc. of alkali at 100° C. A flask provided with a reflux condenser and containing the mixture was heated in a salt bath for exactly 3 hrs. The mixture was then acidified with acetic acid, and the residue filtered off, dried, and weighed.

The "copper number"[8] is also regarded as a measure of the degree of bleaching. This value was obtained by treating 2 g. of pulp with 50 cc. of Fehling solution and boiling under a reflux condenser on a hot plate for exactly 15 min. The residue was then filtered off on an alundum crucible and washed free from alkali. The copper oxide was dissolved in nitric acid (10.7 per cent) and the amount of copper determined by titration with thiosulfate solution under standard conditions.[9]

The cellulose isolated by the chlorination method was examined for α-, β- and γ-cellulose by treatment with caustic soda solution of mercerizing strength (17.5 per cent NaOH).[10] Weighed amounts (approximately 2 g.) of cellulose were treated with a volume of alkali amounting in cc. to ten times the weight of the cellulose and allowed to stand for exactly 30 min. at room temperature with frequent agitation. The alkali was then diluted with an equivalent volume of water and the undissolved residue filtered on an alundum crucible. The α-cellulose, which remained on the crucible, was washed free from alkali with the aid of dilute acetic acid, dried, and weighed. The filtrate was acidified with acetic acid and heated on a water bath to coagulate the β-cellulose, which was then filtered off, washed thoroughly, dried, and weighed. The portion of the cellulose permanently dissolved was γ-cellulose.

MATERIALS INVESTIGATED

The cotton samples examined consisted of

1—Raw linters containing about 20 per cent of hulls.
2—Non-medicated commercial absorbent cotton.
3—Purified linters prepared by cooking raw linters with 20 per cent of their weight of sodium hydroxide at a concentration of 2.6 per cent.
4—Pulped linters prepared by cooking raw linters with a lime-soda-ash liquor containing approximately 8.8 lbs. of caustic soda to 100 lbs. of raw linters.

The wood cellulose samples analyzed were prepared by Messrs. S. D. Wells and V. P. Edwards of the Section of Pulp and Paper of the Forest Products Laboratory by varying the usual cooking conditions somewhat. White spruce (*Picea canadensis*) was the raw material used in all the cooks. Bleached samples were prepared from each of the pulps by subjecting them to the varying amounts of bleaching powder indicated in the tables. The bleaching was carried out at a temperature not exceeding 38° C. and allowed to continue to exhaustion of the bleaching solution. A summary of the yields of bleached and unbleached pulps is given in Table I.

The analytical data obtained on these samples are given in Table II. In the case of the sulfite pulps the letters L and W indicate light, or raw cooked, and well, or normal cooked pulps, respectively. R indicates the pulp has been recooked with a weak (1 per cent) caustic soda liquor. In the soda and sulfate runs, L indicates a light or normal cooked pulp, while W indicates a well or severely cooked pulp.

The samples were air-dried in the form of paper and the material prepared for analysis by running it through a shredder which gave a fluffy product with the individual fibers more or less separated.

DISCUSSION OF RESULTS

MOISTURE—Those values were determined for the purpose of obtaining a basis on which to calculate the results of the other determinations. The samples were exposed long enough to be air-dried at 68° F. in an atmosphere having a relative humidity of approximately 25 per cent.

Wood cellulose obtained by acid cooking is more hygroscopic than that from alkaline treatment, although the reverse has been observed for cotton cellulose.[11] The unbleached sulfite pulps are more hygroscopic than raw linters and absorbent cotton, while the alkaline pulps, except the light cooked sulfate, are less hygroscopic. Bleaching decreases the hygroscopicity of the sulfite pulps but increases the affinity for water of pulps that have been subjected to alkaline treatment.

ASH—All celluloses retain a certain amount of the mineral constituents contained in the original raw material, irrespective of the method employed in their isolation. Schorger[12] found cellulose from spruce wood to contain an average of 0.30 per cent ash. Purified cotton yields an ash ranging from 0.10 to 0.50 per cent, while raw cotton contains 1 per cent or more of mineral constituents.[13] The ash values in the wood

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[7] [illegible] **1905** 10, III 39[illegible]

[8] [illegible] 1911 [illegible]

[9] [illegible] 34 [illegible]

[10] [illegible] 1905 10, III [illegible]. [illegible] 1916 [illegible] 1911, [illegible]

[11] Schwalbe, "Chemie der Cellulose," **1911**, 13.

[12] THIS JOURNAL, **9** (1917), 556.

[13] Schwalbe, "Chemie der Cellulose," **1911**, 34.

TABLE II

SAMPLE NUMBER OR DESIGNATION	Bleaching Powder (35 Per cent Available Cl), Per cent	Moisture	Ash	Cold-Water-Soluble 48 Hrs.	Hot-Water-Soluble 3 Hrs.	Alkali-Soluble 1 Per cent NaOH 1 Hr.	Acetic Acid by Hydrolysis	Ether Extract	Pentosan	Methylpentosan	Furfural	Alkali-Soluble 7.14 Per cent NaOH 3 Hrs.	Methoxy Groups (CH₃O)	Cellulose	IN CELLULOSE					Furfuroids	Lignin (Noncellulose)	G. Cu per 100 G. of Sample
															α Cellulose	β-Cellulose	γ-Cellulose	Pentosan	Methyl-pentosan			
Spruce sulfite pulp, air-dried, results expressed in per cent, calculated on oven-dry (105° C.) weight of pulp[1]																						
Spruce wood	0.00	..	0.31	1.12	2.14	11.57	1.59	1.36	10.39	3.55	..	..	5.30	61.85	..	..	..	9.63	0 72	..	..	..
221 L	0.00	7.99	1.72	2.54	2.76	9.77	0.24	2.10	5.43	3 03	4.15	26.46	2.26	82.72	83.50	0.31	16.19	6.97	1.48	4.43	11 92	2.18
223 L	25.00	6.44	1.36	1.53	3.98	18.14	0.03	0.63	7.07	1.75	4.63	26.93	1.58	87.13	83.70	2.32	13.98	7.07	1.04	4 29	4 08	3.50
224 L	50.00	6.19	1.21	2.15	3.57	16.21	0.02	0.66	6.67	1.63	4.32	26.36	0.72	93.18	83.25	3.39	13.36	6.06	1.11	3.75	0 46	3.04
231 LR	0.00	4.86	1.41	0.30	0.00	1.52	0.05	0.55	4 55	1.14	2 93	5.84	0.58	96.75	85.95	1.71	12.54	4 10	0 84	2 51	2 75	0 95
232 LR	3.00	4 80	1.57	0.68	0.58	2.97	0.08	0.97	3.95	1.19	2.59	6 70	0.35	94.78	94.45	2.46	3.09	4.28	0.95	2 65	3.01	1 12
233 LR	5.00	4.66	1.73	1.21	1.68	3.89	0.11	1.04	3 91	1 21	2 60	8.72	..	94.29	94.49	2.16	3.35	5 09	1.68	3 36	2.82	1 36
234 LR	8.00	5.32	1.78	0.83	1.13	4.62	0.08	0.77	4.17	1 35	2.76	12.41	..	95.60	92.15	3.51	4.34	4.17	2.02	2.93	1.95	1.84
235 LR	12.00	4.94	1.91	1.51	2.41	8.36	0.09	1.57	4.49	1.18	2.96	21 26	..	93.30	89.05	5.97	4.98	4.29	1.26	2.75	1.15	2.53
221 W	0.00	5.59	0.49	0.84	1.24	5.67	0.09	1.45	4 94	1.64	3 31	19.89	1.06	94.95	87.60	2.98	9.42	5.14	1.55	3.39	1.99	2.42
223 W	6.00	5.03	0.78	0.39	0.87	12.35	0.12	1.20	5.74	1 06	3.60	19.89	0.65	96.33	88.25	2.53	9.22	5.63	2.43	3.92	1.14	2.62
224 W	12.00	5.11	0.58	0 30	0.76	11.74	0.20	1.13	5.90	1 16	3 72	23.70	0.55	97.01	87.12	3.91	8.97	4.78	1.76	3.22	0.66	2.47
225 W	20 00	5.17	0.91	1 22	1.54	18.27	0.32	0 76	5.96	1.25	3 76	32.76	0.53	98.89	83.25	7.93	8.82	5 53	1.98	3.73	0.13	3.83
231 WR	0 00	4 41	0.75	0.29	0.12	0.14	0.02	0.73	2.61	1 04	1.76	3.63	0.21	98.17	90.20	2.49	3.00	2.34	0.88	1.51	0.96	1.12
232 WR	2 00	4.61	0.78	0.23	0.51	2.06	0.06	0.64	2.48	0 62	1.54	5.31	0.37	98.10	95 10	1.90	7.31	2.35	1.55	1.70	1.04	1.20
233 WR	5.00	5 18	1 01	0.00	0.28	4.17	0.00	0.72	2.51	0.69	1.60	12.81	..	98 07	93.30	3.84	2.86	2.36	1.17	1.83	0.59	1.93
234 WR	7.00	5 26	0 87	0 41	0.54	7.03	..	0.61	2.65	0.75	1.69	20.02	..	97 68	90.00	7.73	2.27	2.22	1.09	1.50	0.49	2.69
235 WR	12.00	5 34	1 00	0.93	1.76	16.38	..	0.53	3.35	0.80	2.10	36.87	..	95.61	74.80	21.20	4.00	2.33	1.19	1.59	0.44	6.92
Cotton, air-dried, results calculated on oven-dry (105° C.) weight of material analyzed																						
Raw linters	0.00	4.13	1 57	2 00	2.27	7.67	0.16	0.50	1.58	0.52	0.98	12.22	0.36	89.75	83.19	1.87	14.95	0.46	0.32	0.20	8.15	4.55
Absorbent cotton	0.00	4 34	0.11	0.00	0.00	1.75	0.04	0.31	0.58	0.48	0.30	6.20	0.39	98.93	87.60	12.20	0.12	0.50	0.85	0.16	0.36	1.13
Purified linters[3]	2 3	2.67	0 52	0.33	0.23	1.52	0.10	0.24	1.11	0.46	0.63	3.72	0.37	99.32	97.40	2.60	0.00	0.45	0.77	0.30	1.35	0.87
Pulped linters[3]	6–8	2.25	0.64	0.50	0.38	6.46	0.04	0.28	1.97	0.70	1.27	16.67	0.31	97.90	88.30	11.7	0.00	1.31	1.03	0.88	0.12	2.57
Spruce soda and sulfate pulps, air-dried, results calculated on oven-dry (105° C.) weight of pulp																						
201 L-Soda	0	3.91	1.12	0.71	0.26	2.81	0.07	0.49	7.77	1.14	4.82	5.93	0.89	93.17	85.66	7.81	6.53	7.31	1.52	4.59	4.03	1.59
202 L Soda	12	6.26	0.92	0.58	1.07	4.93	0.06	1.10	8.24	1.18	5.09	12.03	0.57	94.26	60.57	34.19	5.24	7.45	1.33	4.63	5.86	1.76
203 L-Soda	20	5 79	0 90	1 27	1.21	6.92	0.04	0.71	8.20	1.35	5.12	17.06	0.32	94.77	53.01	35.07	11.92	6.80	1.50	4.32	4.55	2.40
201 W Soda	0	3 48	0 90	1.27	0.62	2.46	0.06	0.41	3.82	1 25	2.54	5.89	0.47	96.20	80.30	13.27	6.43	3.42	1.54	2.33	2.11	1.09
203 W Soda	7	4 94	0.91	0.51	0.08	3.40	0.06	0.52	3.98	1.66	2.76	7.14	0.26	97.16	55.93	34.22	9 85	3.87	1.88	2.71	2.66	1.66
205 W Soda	15	5.66	1.22	0 45	0.18	9.81	0.04	0.76	4.09	0.63	2.54	22.15	0.29	97.05	51.50	37.80	10.70	3.41	1.92	2.48	2.22	3.61
211 L Sulfate	0	4 89	1 16	1.25	0.40	2.62	0.10	1.65	10.04	0.92	6.09	8.61	0.68	94.56	84.20	6.31	9.49	9.96	1.29	6.10	3.39	1.38
212 L-Sulfate	10	6 04	1.27	0 59	0.00	3.61	0.04	1.42	10.07	0.64	6.05	11.64	0.26	94.00	64.70	23.98	11.32	8.30	1.70	5.26	5.53	1.67
213 L-Sulfate	25	5 97	1.40	1.23	0.91	14.02	0.04	1.10	9.90	0.85	6.00	31.04	0.25	94.56	56.87	31.55	11.58	8.46	1.46	5.27	4.04	3.93
211 W-Sulfate	0	3.64	1.01	1 23	0.82	2.18	0.06	0.63	6.05	1.07	3.79	5.51	..	96.17	81.80	10.31	8.07	5.81	1.62	3.85	1.88	1.46
213 W-Sulfate	6	5.74	0.83	0.00	0.00	2.28	0.03	0 89	7.67	1.35	4.51	7.10	0.24	95.68	72.20	18.72	9.08	6.95	1.01	4.28	3.43	1.58
214 W-Sulfate	15	5.49	1.21	0.00	0.00	8.51	0.04	0.93	7.17	1.62	4.22	20.47	0.18	95.40	62.95	26.90	10.15	6.20	0.97	3.84	2.64	2.98

[1] The values given except those in the column headed "In Cellulose," are averages of two closely agreeing duplicates.

[2] Values obtained by Schorger, THIS JOURNAL, **9** (1917), 556.

[3] The low moisture content of these two samples is due to their having been dried over a steam-heated radiator.

celluloses examined, while fairly uniform for each series, are high compared to spruce wood on the one hand and to purified cotton on the other. The high values are undoubtedly due to insufficient washing of the pulps and to tendency of cellulose to absorb mineral salts.

WATER-SOLUBLE CONTENT—Cellulose is generally regarded as insoluble in water.[14] While the water-soluble content of the samples analyzed may be accounted for in part by soluble salts retained from previous treatments, many of the samples show appreciable amounts of water-soluble material which cannot be accounted for in this way. The wood celluloses isolated appear to contain more water-soluble material than the treated cotton cellulose. The sulfite pulps are more soluble in hot than in cold water under the conditions of these experiments, while the reverse is true of the pulps from alkaline treatment. Bleaching increases the solubility of the sulfite pulps but tends to decrease the solubility of the soda and sulfate pulps. Cross and Bevan[15] have recently shown that cotton cellulose is changed both qualitatively and quantitatively by contact with water.

ALKALI-SOLUBLE CONTENT—The solubility test in 7.14 per cent sodium hydroxide is in reality an alkali-acid solubility test, since the alkaline solution is acidified before filtering. This almost invariably results in the precipitation of some material (probably analogous to β-cellulose) which would otherwise remain in solution. Notwithstanding this difference in procedure, the values for solubility in 1 per cent alkali and 7.14 per cent alkali parallel each other in practically all cases.

In general, increased solubility in alkali results from increased bleaching, but notable exceptions to this are found in the case of the light or raw-cooked (Series 221 L) sulfite pulp. The results obtained in the light-cooked series, where no increase in solubility occurs on bleaching, are due to two compensating changes which take place. As indicated by the lignin values, bleaching removes the noncellulose material, which is more or less soluble in alkali, on the one hand, and produces alkali-soluble constituents from the residual cellulose, on the other. The effect is a practically constant percentage of alkali-soluble material with 7.14 per cent sodium hydroxide. With 1 per cent alkali, the two changes do not compensate so closely but their effect is quite apparent.

Several of the recooked samples which have been lightly bleached, together with both of the soda pulps and the well-cooked sulfate pulp, approach purified linters and absorbent cotton in their degree of solubility in alkali. In general, however, the wood celluloses are more soluble than cotton cellulose which has been subjected to corresponding treatment.

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[14] Schwalbe, "Chemie der Cellulose," 1911, 19.

[15] "Cellulose," **1918**, 311.

The solubility in 7.14 per cent sodium hydroxide is apparently due to the presence of lignin, furfural-yielding constituents, and γ-cellulose in the pulp and also to the conversion of some of the more resistant celluloses into soluble form during the 3-hr. boiling with the alkali in the test. Evidence for this is given in Table III, where the solubility in alkali on the one hand is compared with the β- and γ-cellulose and loss on chlorination on the other. In the alkaline pulps the conversion of insoluble to soluble cellulose has apparently reached its limit in the original cook.

TABLE III

SAMPLE NO.	7.14 Per cent NaOH Soluble Per cent	β- and γ-Cellulose[1] Per cent	Loss on Chlorination Per cent
221L	26.46	17.18	17.18
223L	26.93	13.97	12.87
224L	26.36	15.61	6.72
221W	19.89	11.78	5.05
223W	19.89	11.31	3.67
224W	23.70	12.49	2.99
225W	32.76	16.06	4.11
231WR	3.63	9.85	1.87
232WR	5.31	4.81	1.90
233WR	12.81	6.57	1.93
234WR	20.02	9.00	2.32
235WR	36.87	21.09	4.39
Munition linters	3.72	2.58	0.68
201L Soda	5.93	13.36	6.83
201W Soda	5.89	18.95	4.80
211L Sulfate	8.61	14.94	5.44
211W Sulfate	5.51	17.68	3.83

[1] Calculated on the basis of the original pulp.

If time and temperature of treatment and strength of alkali were the same in the alkali-solubility determination and in the determination of α-, β-, and γ-cellulose the sum of Columns 2 and 3 would more nearly approximate Column 1. That the 7.14 per cent solubility figures are in the main greater than this sum in the case of the sulfite pulps, especially those which have not been redigested, indicates that this solubility test is too severe a test for these pulps as considerable of what is determined as α-cellulose is dissolved during the test.

ACETIC ACID BY HYDROLYSIS—Spruce wood yields on hydrolysis with dilute sulfuric acid 1.59 per cent of fatty acids consisting almost entirely of acetic acid. The data show the acetyl groups producing this acid to be removed both by acid and alkaline cooking. Acetic acid residues, if present in the wood, are not resolved by subsequent cooking or bleaching into a condition in which they yield acetic acid on further hydrolysis with dilute sulfuric acid. The recooked sulfite pulps and also the soda and sulfate pulps correspond with cotton in yielding practically no acetic acid by hydrolysis.

ETHER EXTRACT—This extract contains the waxes, fats, resins, etc., not removed from the pulps by cooking. Spruce wood yields an extract of 1.36, while subjecting this wood to mild acid cooking tends to concentrate the extractive material in the pulp, as is shown in Sample 221L. Strong bleaching, however, tends to reduce the amount of extractives in the sulfite pulps but does not cause an elimination of them beyond a certain point, as indicated in the well-cooked series. The cottons yield smaller amounts of extractive materials than the woods. Soda cooking is slightly more efficient in removing these materials than sulfite or sulfate cooking. Subsequent bleaching of the soda and sulfate pulps, in contrast with the sulfite pulps, does not remove any of the residual extractives. In fact, the percentage of ether-soluble constituents appears to be slightly increased by the action of bleaching powder on the alkaline pulps. The two soda cooks are nearest the maximum specification of 0.4 per cent of extractive matter for cotton, but none of the samples of pulp meets this requirement.

PENTOSAN, METHYLPENTOSAN, AND FURFURAL—The furfural- and methylfurfural-yielding constituents of wood are usually calculated in terms of pentosan and methylpentosan. This procedure was followed in tabulating the present results. Since the extraction of methylfurfural phloroglucide with alcohol is not entirely satisfactory, the results are also calculated in terms of furfural, which eliminates the effect of this extraction in the data recorded under the heading of "Furfural" and gives values more comparable than the values under the other two headings. In general, however, the values in all three columns parallel each other rather closely.

The chief source of furfural in woods are the pentosans, although the lignin also contains furfural-yielding constituents. In pulps there may be present hydrocellulose and oxycellulose which also yield furfural. Since the yield of furfural from each series of pulps is constant or nearly so the indication is that very little hydrocellulose or oxycellulose is formed during bleaching. This seems to show that the solubility of the pulps in alkali, which increases rapidly with increased bleaching, and which is usually attributed to the above modifications, is due to some other change in the cellulose.

The pulps contain larger percentages of pentosan and methylpentosan than the cottons. To what extent this makes them less suitable than cotton for esterification has not been fully determined, although it is commonly considered that, in cellulose for nitration, the presence of lower carbohydrate bodies leads to a less stable nitration product.

METHOXY CONTENT—Methoxy groups are characteristic of the lignified celluloses. They are contained chiefly in the lignin and are therefore largely removed by cooking and by bleaching. The absence of methoxy groups is regarded as an indication of a very pure form of cellulose. The bleached soda pulps and the recooked sulfite pulps compare very favorably with the cottons which are shown to contain very small amounts of methoxy. Benedikt and Bramberger[16] found no methyl groups in cotton but small amounts in sulfite cellulose.

CELLULOSE—The yields of cellulose from the pulps by the chlorination method more nearly approach those from cotton in the case of the recooked, normal cooked sulfite pulp and the well-cooked soda and sulfate pulps. There is, however, considerable difference in the nature of these celluloses when the α-, β-, and γ-celluloses and furfural-yielding constituents in them are considered. The γ-cellulose for each series of bleached pulps is fairly constant but is less than that for the unbleached pulps of the same series in the case of the sulfite pulps and greater in the case of the soda and sulfate pulps. All the wood celluloses contain more γ-cellulose than the purified cotton samples. In the manufacture of nitrocellulose γ-cellulose is said to be lost during nitration[17] and therefore reduces the yield of nitrocellulose obtained.

Pulps obtained by the alkaline cooks contain a higher percentage of β-cellulose than those obtained by the acid cooks. Mild bleaching has little effect but heavy bleaching converts α- into β-cellulose. Upon nitration β-cellulose is said to give a less stable product, but the evidence on this point is not conclusive.

Furfuroids, as pointed out by Cross and Bevan,[18] appear to be normal constituents of cellulose isolated from wood. This differentiates wood cellulose from cotton cellulose, although the data show that the latter contains small amounts of furfural-yielding constituents.

The sample which is the nearest approach to the purest cotton sample (purified linters) from the standpoint of the

[16] *Monatsh.*, **11**, 260.

[17] THIS JOURNAL, **12** (1920), 382.

[18] "Cellulose," **1918**, 83.

nature and yield of cellulose is the recooked normal cooked sulfite pulp (232 WR) bleached with 2 per cent bleach.

LIGNIN—The term lignin is rather indefinite and is commonly applied to that portion of wood which is not cellulose. In this paper lignin is defined as the residue insoluble in 72 per cent sulfuric acid under the conditions already outlined. The values given are not corrected for ash since the ash content for each series of samples is practically constant.

A stronger concentration of acid is sometimes employed in this determination. However, we obtained higher values using 95 per cent sulfuric acid, as indicated by the following figures:

	72 Per cent H_2SO_4		95 Per cent H_2SO_4	
SAMPLE NO.	Per cent	Mean	Per cent	Mean
231WR	1.05		1.65	
	0.88	0.96	1.65	1.65

The procedure in making the determinations with 95 per cent sulfuric acid was to treat the sample for 5 min. with ten times its weight in cc. of acid. The reaction mixture was then diluted to twenty times its volume and boiled under a reflux condenser for 4 hrs. The high values obtained are probably due to a certain amount of charring of the cellulose.[19]

Soft woods like spruce contain approximately 25 to 30 per cent lignin which, as shown by the data, is removed to a greater or less degree in the pulping process, depending upon the severity of cooking conditions and the nature of the process employed. The effect of bleaching in removing lignin from sulfite pulp is well indicated in each of the series of bleached samples, but particularly in the case of the raw-cooked sulfite samples (Series 221L). On the other hand, the inability of bleaching to remove the lignin from alkaline cooked pulp is well illustrated in the soda and sulfate samples. Bleaching appears to increase rather than decrease the amount of material insoluble in sulfuric acid. The well-cooked sulfite pulps give values that agree well with those for cotton, but the pulps obtained by alkaline cooking run rather high in lignin.

COPPER NUMBER—The copper number was proposed by Schwalbe as a means of measuring the degree of bleaching of cellulosic materials and a detailed method of procedure was worked out in his laboratory for making the determination. The simpler method employed in this investigation, as already outlined, gives comparable results and is less tedious than the original method. Blank runs on Fehling solution gave an average value of 0.38, which was assumed to be constant and the values were not corrected for it.

The values obtained increase with increasing amounts of bleach employed, but the unbleached samples also yield values of nearly the same magnitude as the mildly bleached pulps showing that products other than those produced in bleaching also reduce Fehling solution. Bancroft[20] concluded that the reducing action on Fehling solution is probably not characteristic of oxycellulose, to which it is in part attributed, but to decomposition products of the cellulose.

The differences in the copper number with increased bleaching are not so pronounced as the corresponding differences in the alkali solubility. The latter constant appears, therefore, to be more suitable as a means of determining the degree of bleaching than the copper number. The usual specification of a copper number not to exceed 1.0 would exclude all of the pulps except 231LR.

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[19] *Z. physiol. Chem.*, [7] **83** (1882), 913.

[20] *J. Phys. Chem.*, **19** (1915), 159.

A Reagent-Bottle Siphon[1]

By C. A. Jacobson

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THE accompanying cut shows the construction of a buret siphon, especially suitable for use with reagent bottles. The siphon is so constructed that a measured quantity of the liquid may be removed from the bottle without pouring or applying suction by mouth.

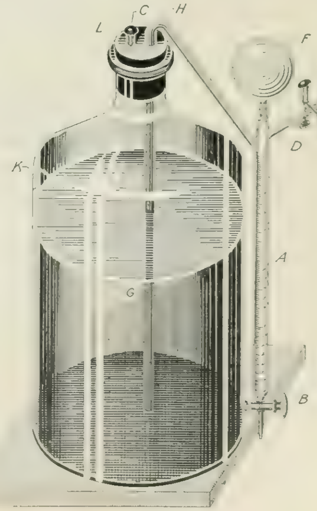
It is composed of a buret arm, A, calibrated in cubic centimeters from 0 to 25, and a heavy glass arm, G, which is supported in a bottle, K, by the stopper L. The upper end of A is drawn out to receive a rubber bulb, F, of a slightly larger capacity than the buret. The side tube D is provided with a rubber tube E and pinch clamp. The lower end of A is drawn out like the delivery end of a buret and provided with a stopcock, B. C is a glass plug which must be removed before withdrawing liquid from the bottle.

To start the siphon, close B, open E, compress the bulb F, clamp E, then release the pressure on F, and the bulb will draw the liquid through G into A. If it is desired to withdraw a large quantity of the liquid from the bottle, let the entire tube up to H, fill with liquid. When B is opened the liquid siphons over. To stop the siphoning open E.

If it is desired to measure out a small quantity of the liquid, repeat the above directions, but, before the arm H fills with liquid, open E, and keep open while adjusting the height of the liquid in A, by means of the stopcock.

This reagent-bottle siphon can now be obtained in a 2-l. size; other sizes could doubtless be supplied also.

The writer has used a similar siphon for several years and finds it very convenient. An additional support for the buret arm could be arranged without much difficulty, but experience shows that this would be quite unnecessary. However, when the stopcock B is made shorter than the glass collar, a rubber band passed around the lower end of the bottle and around the buret just above B would furnish ample support for the siphon.



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[1] Received May 16, 1922.

The Separation of *m*- and *p*-Cresols from Coal-Tar Crude Carbolic Acid[1]

By Arthur Fred Campbell

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A method is described for the separation of practically pure m- and p-cresols from coal-tar crude carbolic acid.

A preliminary separation of the 59 to 60 per cent m-cresol product may be obtained by the comparative difference in the rates of sulfonation of the two cresols at a low temperature. The most favorable conditions are preferential sulfonation at 40° C. with 96 per cent sulfuric acid for 6 hrs. The extracted aqueous sulfonic acid liquor yields an approximately 80 per cent m-cresol product.

A 98 to 100 per cent m-cresol is obtained on conversion of the extracted aqueous sulfonate of mono-sulfonic acids into their ammonium salts and crystallization of the latter.

An 88 to 90 per cent p-cresol is obtained by a second preferential sulfonation of the above-extracted nonsulfonated cresols, and recovery and purification of the residual nonsulfonated p-cresol product.

THE object of this paper is to describe a method for the separation of practically pure *m*- and *p*-cresols from the crude carbolic acid obtained by the usual works practice in the coal-tar industry.

The crude carbolic acid separated during the distillation and working up of coal tar contains varying amounts of phenol and cresols, largely dependent upon the kind of tar, its source, and the method of distillation.

In the absence of any great demand for pure cresol products, commercial fractionation is usually limited to the production of:

1—Distillates rich in phenol, from which carbolic acid crystals may be obtained by crystallization

2—Fractions of high boiling point, containing little phenol and consisting largely of the three cresols.

In many cases the latter fraction also contains varying proportions of the xylenols.

The usual products manufactured by the tar distiller, who does not proceed to the further separation and purification of phenol and the cresols, are the various grades of carbolic and cresylic acids. These products may be obtained either by the fractional washing of the crude tar oils with caustic soda or by the fractional distillation of the mixture of phenol, cresols, and xylenols recovered in one stage by treatment with caustic soda.

Although homologous substances may, in general, be separated by fractional distillation, the method is not so widely applicable to the separation of isomerides. It is possible, however, on the basis of the boiling-point differences, to separate by fractionation the complex crude carbolic acid into fractions which consist for the most part of (1) phenol, (2) *o*-cresol, (3) *m*- and *p*-cresols, and (4) xylenols and other [illegible]

Since *m*- and *p*-cresols are isomerides, the differences in their physical properties will be very small. By taking advantage of differences in their chemical behavior, however, it is possible to separate, in a pure state, the third fraction into the two isomers, *m*- and *p*-cresol.

Many methods for the separation have been published. The more important of these references are listed below.[2]

The following summary shows the differences given by the various authors for the physical properties of phenol and the three cresols:

	Phenol	Cresol Ortho	 Meta	 Para
Fox and Barker [*J. Soc. Chem. Ind.*, **36** (1917), 842; **37** (1918), 269T]				
Boiling point, ° C.	182.2	191.8	202.1	202.5
Freezing point, ° C.	40.5	30.1	....	36.0
Specific gravity, 15.5° C	...	1.0516	1.0387	1.0388
Refractive index, n_D at 40° C	...	1.53719	1.53322	1.53187
Dawson and Mountford [*J. Chem. Soc.*, **113** (1918), 937]				
Freezing point, ° C.	41.0	30.45	10.0	34.15
Specific gravity, 25°/4°	1.0710	1.0415	1.0295	1.0295
Viscosity, *n*, 25° C.	0.0883	0.0762	0.1240	0.1413
Sidgwick, Spurrell and Davies [*J. Chem. Soc.*, **107** (1915), 1202]				
Solubility in H_2O at 20° C., per cent	8.5	2.8	2.3	2.0

At the time of this research the methods published for the estimation of phenol and the three cresols were very unsatisfactory, and were practically adaptable only to the individual pure products and not to the complex mixtures under consideration in this paper. Those published for phenol were assigned chiefly to serve as an examination of pharmaceutical phenol, and with a mixture of the three cresols it was possible to estimate only *m*-cresol with any degree of accuracy. A considerable number of original papers on the estimation of phenol and the three cresols have since been published.[3]

Upon investigation of the published methods for the separation of *m*- and *p*-cresol it is apparent that the most satisfactory and economical separation of the two isomers in a pure state is by a sulfonation method. If *m*- and *p*-cresols have under certain definite conditions widely different rates of sulfonation it will be possible to obtain a partial separation.

It was therefore considered desirable to determine the possibilities of a method based on a preferential sulfonation of the crude *m*-*p*-cresol product, and at the same time to eliminate, if possible, the recovery from the sulfonic acids of an unsatisfactory and only partly purified cresol product.

If the sulfonate from a preferential sulfonation is utilized, without decomposition of the sulfonic acids with steam and recovery of the cresols in the usual manner, it will be an additional advantage to sulfonate under such conditions that only monosulfonic acids are formed, thus avoiding difficulties in crystallization due to complex solubility curves.

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[1] Received [illegible]

[2] Riehm, D. R. P. 53,307 (1889); Byk, D. R. P. 100,418; Rud Rütgers, D. R. P. 137,584, 141,421; Fr. Patent 317,512; Brit. Patent 286 (1902); Vidal, Fr. Patent 315,695 (1901); Chem. Fabr. Ladenburg, D. R. P. 148,703; Brit. Patent 1881 (1904); Schulze and Ladenburg, D. R. P. 152,652; Bayer & Co., D. R. P. 156,761, 157,616; Brit. Patent 9953 (1904); Raschig, D. R. P. 112,545; U. S. Patent 655,117; Brit. Patent 18,334 (1899); Raschig, D. R. P. 114,975; U. S. Patent 656,263; Brit. Patent 25,269 (1899); Hoffmann-Laroche & Co., Fr. Patent 434,534 (1911); Brit. Patent 25,166 (1911); Fr. Patent 434,643 (1912); U. S. Patents 1,025,615, 1,025,616; Brit. Patents 2458 (1912), 3923 (1912); Schülke and Mayr, D. R. P. 268,780 (1911); Terrisse, Fr. Patent 444,187 (1912); D. R. P. 267,210; Terrisse, Fr. Patent 463,221 (1913); D. R. P. 281,054; Darzens, Brit. Patent 107,961 (1916); Downs and Potter, U. S. Patent 1,364,547.

[3] Masse and Leroux, *Compt. rend.*, **163** (1916), 361; Weiss and Downs, This Journal, **9** (1917), 569; Skirrow, *Ibid.*, **9** (1917), 1102; Knight, Lincoln, Formanek, and Follett, *Ibid.*, **10** (1918), 9; Fox and Barker, *J. Soc. Chem. Ind.*, **36** (1917), 842; **37** (1918), 265T; Sharples, *Ibid.*, **37** (1918), 109T; Kendall and Beaver, *J. Am. Chem. Soc.*, **43** (1921), 1853.

The results of the preferential sulfonation experiments show that a fairly satisfactory preliminary separation of the crude *m*-*p*-cresol may be obtained by sulfonation at a temperature of 30° to 40° C. with 96 per cent sulfuric acid for 6 hrs. After the extraction of the nonsulfonated cresols, an aqueous solution of the monosulfonic acids of *m*- and *p*-cresol is obtained, with the *m*-cresol content varying from 70 to 80 per cent according to the composition of the crude material.

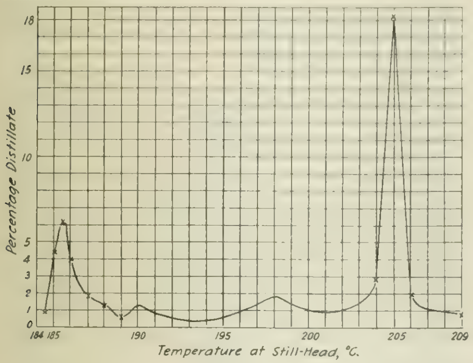

Fig. 1

By the preferential sulfonation of an approximately 60 per cent *m*-cresol product, followed by conversion of the extracted aqueous solution of the monosulfonic acids into the ammonium salts, and crystallization of the latter at a known concentration, a 98 to 100 per cent *m*-cresol product may be obtained. A product containing 87 per cent *m*-cresol is similarly obtained from a crude 50 per cent *m*-cresol.

It follows from the method outlined for the separation of *m*-cresol, together with the fact that *p*-cresol is sulfonated at only approximately one-third the rate of *m*-cresol under the specified conditions, that the greater part of the *p*-cresol is contained in the nonsulfonated cresols recovered from the *m*-cresolsulfonate. Although the nonsulfonated material, containing *p*-cresol equivalent to 80 to 85 per cent of the amount in the crude 60 per cent meta product, is an excellent basis for the separation of para, it is not a mixture of pure *m*- and *p*-cresols but contains a small percentage of *o*-cresol and certain of the xylenols.

Since the comparative speed of sulfonation of *o*-cresol is, under the chosen conditions, only 0.60 times that of *m*-cresol, the small amount of *o*-cresol will be accumulative in the nonsulfonated cresols. Similarly, *m*-cresol is sulfonated at 3.02 times and 1.260 times the rate of pure asymmetric *m*-xylenol ($OH : CH_3 : CH_3 = 1 : 2 : 4$) and pure *p*-xylenol ($OH : CH_3 : CH_3 = 1 : 2 : 5$), respectively, and these products will also be accumulative. The xylenols are of special interest since they occur in the coal-tar fractions allied to the more important cresol fractions.

The small percentage of hydrocarbons in the 60 per cent *m*-cresol product remains practically unchanged and will also accumulate in the nonsulfonated cresol product.

A high percentage *p*-cresol may, however, be obtained by the resulfonation of the nonsulfonated cresol product with the requisite quantity of sulfuric acid. The second nonsulfonated cresol product yields, on removal of the hydrocarbons and further purification by freezing and draining under vacuo, an 88 to 90 per cent *p*-cresol.

Experimental

The crude *m*-*p*-cresol product used in this research was obtained by the fractional distillation of crude carbolic acid, consisting of phenol, *o*-, *m*-, and *p*-cresols, and the mixed xylenols, as produced in the usual works practice.

The dehydrated crude carbolic acid with a phenol content of 17 to 18 per cent gave the following distillation points when distilled from a Wurtz flask:

First drop	191° C.
10 per cent	194
20	195.5
30	198
40	200
50	201
60	203.5
70	211.5
80	219
90	246
Dry	292
Sp. gr. 60°/60°	1052

The results of the distillation, made with an efficient fractionation column packed with small metal rings, are shown in Figs. 1 and 2, where the percentage distillate and percentage *m*-cresol in distillate, respectively, are plotted against the temperature in ° C., corrected for barometric pressure and emergent stem of thermometer, read at the still-head.

The author desires to express at this point his appreciation to H. S. Land and J. H. Roebuck for assistance in the experimental part of this paper.

Preferential Sulfonation of *m*- and *p*-Cresols

The author has been unable to find any published work showing the comparative difference in the rates of sulfonation of the cresols.

The influence of the introduction of the methyl group into the phenol molecule and the effect of temperature on the speed of sulfonation of phenols is shown in a paper published independently.[4]

It is well known that reaction speeds are extremely sensible to and readily influenced by variation in temperature. A series of experiments were carried out under various conditions to determine whether *m*- and *p*-cresols have different velocities of sulfonation and, if so, the conditions which give the widest degree of preferential sulfonation. A quantity of sulfuric acid less than is necessary for complete sulfonation will have to be employed to effect a separation. The time of sulfonation will influence the amount sulfonated.

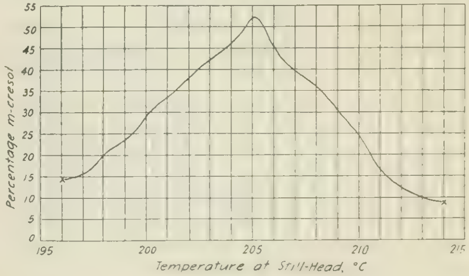

Fig. 2

The crude 59 to 60 per cent *m*-cresol product, used in the majority of the experiments, gave the following points (page 734) when distilled from a Wurtz flask fitted with the bulb of the thermometer on a level with the exit tube, at the uniform rate of 60 drops per min.

The sulfuric acid was gradually added to the *m*-*p*-cresol product over a period of 10 min. During the addition of

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[4] *J. Chem. Soc.*, **121** (1922), 847.

[illegible]	59.7
[illegible]	199.4° C.
[illegible]	201.1
[illegible]	201.8
[illegible]	202.0
[illegible]	202.1
[illegible]	202.3
[illegible]	202.4
[illegible]	202.6
[illegible]	202.8
[illegible]	203.4
[illegible]	203.8

the acid the sulfonation mass was maintained, by cooling or heating, at approximately 1° C. below the desired sulfonation temperature.

The corked flasks were suspended in a water bath with the body of the flask completely immersed. The temperature of the bath was regulated by a thermostat and maintained to within ± 0.5° C. of the desired temperature for 6 hrs. The sulfonation mass was poured into water, the nonsulfonated cresols extracted with pure benzene, the combined benzene extracts washed once with water, and the benzene removed by distillation with a Young's 4-bulb pear column to 160° C. By repeating the distillation three times to 160° C. the residual cresols contained only an infinitesimal amount of benzene.

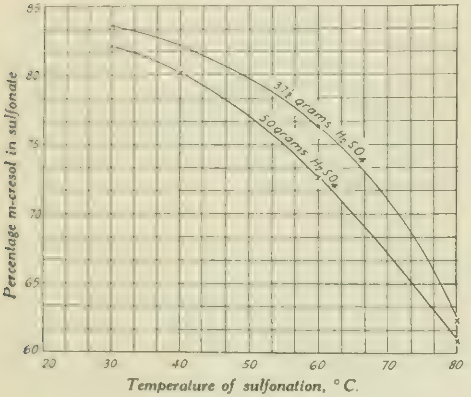

Fig. 3

The weighed extract of nonsulfonated cresols was estimated for *m*-cresol by Raschigs' method[6] and the necessary figures calculated for the nonsulfonated and the sulfonated cresols.

The most important data obtained from a considerable number of experiments using 59 to 60 per cent *m*-cresol and varying amounts of different strengths of sulfuric acid may be summarized as follows:

The weights of different strengths of sulfuric acid necessary to yield a sulfonate of approximately the same composition showed that with acid of less than 96 per cent the amount originally taken was in excess and out of all proportion to the amount actually used in the sulfonation.

The *m-p*-cresol product does not form a homogeneous solution with sulfuric acid of less than 88 per cent, and it is necessary to agitate the mass during the whole period of reaction. Homogeneous solutions are formed with acid of a higher concentration and, after the addition of the acid, agitation is unnecessary. The reaction mass is simply maintained at the desired temperature for the required period.

The results obtained with different amounts of 96 per cent sulfuric acid and 100 g. of the *m-p*-cresol product are diagrammatically represented in Figs. 3 and 4, where the percentage of *m*-cresol in the sulfonated product is plotted against the temperature of sulfonation and the weight of sulfuric acid, respectively.

The results show that at low temperatures there is a decided difference in the comparative rates of sulfonation and that *m*-cresol is sulfonated at a much faster rate than *p*-cresol. Thus at 20° C., under exactly the same conditions, *m*-cresol is sulfonated at almost five times the rate of *p*-cresol. As the temperature increases the difference in the comparative rate of sulfonation diminishes, until a point is reached when the two isomers are sulfonated at practically the same rate.

The percentage of *m*-cresol in sulfonate, with unit time, decreases with increase of weight of 96 per cent acid, and also with increase of temperature.

Although the sulfonate with the highest percentage of meta compound is obtained at comparatively low temperatures, the most satisfactory results, considered from all points of view, are probably those obtained at 40° C.

By taking into consideration (1) the desirability of maintaining a minimum of 70 per cent and 80 per cent *m*-cresolsulfonate from a crude 50 and 60 per cent meta product, respectively; (2) the highest yield of sulfonated cresols compatible with the 70 or 80 per cent *m*-sulfonate; (3) the percentage of original meta compound contained in the sulfonate; and (4) the weight of sulfuric acid necessary to obtain this product, the tabulated results show that although the 30° sulfonate contains a slightly higher percentage meta than the 40° sulfonate, the weight sulfonated and the amount of the original meta contained in the sulfonate are considerably higher at 40° than at 30°.

The results obtained with 50/51 per cent and 59/60 per cent *m*-cresol, using the same weight of acid in each case, (37.5 g. of 96 per cent per 100 g. of crude cresol) for 6 hrs. at 30° and 40° C., respectively, are summarized in the following table:

Crude product, per cent *m*-cresol....	50 to 51		59 to 60	
Temperature, ° C..................	30°	40°	30°	40°
Per cent cresol sulfonated...........	22.8	31.8	28.0	35.8
Per cent *m*-cresol in sulfonate	73.3	70.1	83.6	82.2
Per cent total *m*-cresol in sulfonate .	35.3	47.1	40.0	50.3

The sulfonate, at a temperature higher than 40° C., has a correspondingly lower percentage of *m*-cresol and, as such, is not a suitable basis for the separation of pure *m*-cresol by the method described below.

Approximately 30 per cent more by weight of 96 per cent sulfuric acid is required at 30° than at 40° C. to yield in unit time a sulfonate of similar percentage composition and containing the same amount of original *m*-cresol.

At 40° C., *m*-cresol is sulfonated at approximately three times the rate of *p*-cresol.

The results summarized below show that by sulfonation for 6 hrs. at 40° C., acids of a higher concentration than 96 per cent, with the same weight of actual sulfuric acid in each case, give a sulfonated product with practically the same percentage of *m*-cresol and equivalent to the same total *m*-cresol.

	H_2SO_4		SO_3	SO_3
Strength of acid, per cent..........	96.0	100.0	5.0	10.0
Per cent cresols sulfonated	35.8	35.0	36.0	36.0
Per cent *m*-cresol in sulfonate.......	82.20	83.57	81.25	82.00
Per cent total *m*-cresol in sulfonate..	50.30	49.83	49.83	50.30

It will be seen elsewhere that for any given temperature the velocity of sulfonation is independent of either the amount or strength of acid used in the sulfonation.

Thus the most satisfactory and favorable conditions for a preliminary separation of *m*- and *p*-cresols by preferential sulfonation may be summarized: (1) the crude product must be essentially a mixture of *m*- and *p*- cresol, contain no phenol, and only a small percentage of either *o*-cresol or the xylenols; (2) the sulfonation must be carried out at a low temperature, preferably at 40° C.; (3) concentrated sulfuric acid, preferably 96 per cent and less than the theoretical amount necessary for complete sulfonation; and (4) the sulfonation is allowed to continue for 6 hrs.

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[6] Z. [illegible] 14 [illegible]

It will be seen below that only monosulfonic acids are formed under these conditions.

META-CRESOL

Under the above conditions of sulfonation an aqueous solution of the monosulfonic acids of *m*- and *p*-cresol, with a 70 to 80 per cent meta content varying proportionately to the 50 to 60 per cent meta content in the crude *m*-*p*-cresol product, may be obtained after extraction of the nonsulfonated cresols.

If it is desired, at this stage of the purification, to recover the high percentage *m*-cresol product from the aqueous sulfonic acid solution, this may be conveniently and readily effected by adding the sulfonation mass to a quantity of water which, after extraction to remove the nonsulfonated cresols, merely requires heating to the boiling point (130° C.) to obtain an almost theoretical decomposition of the sulfonic acids. The extracted aqueous liquor at this concentration is equivalent to 60 per cent sulfuric acid.

With a view, however, to the utilization of this aqueous liquor without decomposition of the sulfonic acids, the solubilities of the calcium, barium, sodium, and ammonium salts of the *m*- and *p*-cresolmonosulfonic acids in water at 20° C. were determined. These particular salts were chosen in preference to others since they were the most readily adaptable to commercial practice.

For this purpose 50 g. of the purified cresol were sulfonated with an equal weight of 96 per cent sulfuric acid for 6 hrs. at 40° C. The extracted aqueous solution of the monosulfonic acids was converted into the barium salts, and aliquot portions of the solution of the barium salt, free from carbonate and sulfate of barium, were converted into the sodium and ammonium salts in the usual manner. The calcium salts were prepared through the ammonium salts in order to obtain the salt free from calcium sulfate.

The solubilities are given in g. of anhydrous salt per 100 g. of water at 20° C.

	Meta	Para
Barium	6.68	4.03
Calcium	9.03	6.84
Sodium	7.91	10.10
Ammonium	10.84	19.17

The amount of barium in the barium salts of the above *m*- and *p*-cresolsulfonic acids was estimated as sulfate by (1) incineration of 1 g. of the salt with ammonium nitrate, and (2) the precipitation method, with the following results:

META-SALT

1 g. barium salt gave 0.456 g. $BaSO_4$
1 g. barium salt gave 0.454 g. $BaSO_4$
Mean = 0.4550

PARA-SALT

1 g. of barium salt gave 0.456 g. $BaSO_4$
1 g. of barium salt gave 0.457 g. $BaSO_4$
Mean = 0.4565

The theoretical weight of barium sulfate equivalent to 1 g. of the barium salt of either *m*- or *p*-cresolmonosulfonic acid is 0.4563 g. It may therefore be assumed that only monosulfonic acids are obtained in the above method of sulfonation.

The following additional comparative ratios may be calculated by successively taking as unity (1) the barium salt of the two isomeric monosulfonic acids, (2) the *m*-monosulfonic acid salt, and (3) the *p*-monosulfonic acid salt.

1	Meta	Para
Barium	100	100
Calcium	135	170
Sodium	118	250
Ammonium	162	475
(2) and (3)	*m* : *p*	*p* : *m*
Barium	100 : 60	100 : 166
Calcium	100 : 76	100 : 132
Sodium	100 : 127	100 : 78
Ammonium	100 : 177	100 : 57

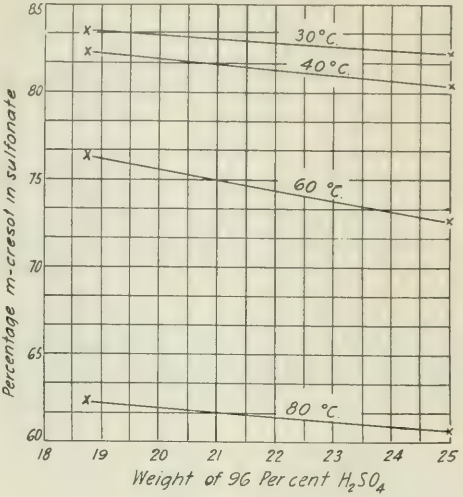

FIG. 4

The solubility determinations show:

1—The alkali salts of the monosulfonic acids of *p*-cresol are more soluble than the corresponding salts of *m*-cresol.

2—The reverse is the case with the alkaline earth salts, and the salts of the monosulfonic acid of *m*-cresol are more soluble than the corresponding salts of *p*-cresol.

3—The barium salts of either monosulfonic acid are the least soluble, while the ammonium salts are the most soluble.

4—The ammonium salts have the widest difference in degree of solubility.

5—The range of solubility of the barium salts is also fairly wide, but not quite so marked, and in the reverse order to the ammonium salts.

Thus a fairly complete separation of the aqueous solution of the *m*- and *p*-cresolmonosulfonic acids may be effected by the conversion of the mixed sulfonic acids into their ammonium salts and a fractional crystallization of the latter. For every 100 parts of the ammonium *m*-salt approximately 177 parts of ammonium *p*-salt would be held in solution at any particular concentration at 20° C.

The results from the fractional crystallization of the ammonium salts of the monosulfonic acids prepared in the above manner from a crude product with an analysis of 59.4 per cent *m*-cresol, 1.3 per cent hydrocarbons, and by difference 39.3 per cent *p*-cresol, will illustrate the degree of separation by this method.

Five hundred grams were sulfonated with 185 g. of 96 per cent sulfuric acid at 40° C. for 6 hrs. The sulfonation mass was poured into 750 cc. of water, and the extracted aqueous solution of the monosulfonic acids was converted, through the barium salts, into the ammonium salts. The final filtered mother liquor was evaporated to 1.190 sp. gr.

at 60° C. which concentration yielded a reasonable amount of first crop crystals at 20° C.

The crystals were filtered, drained on the pump, and pressed between filter paper in a small hand hydraulic press to remove as much of the adhering mother liquor as possible. The crystal was decomposed by the addition of half its weight of concentrated sulfuric acid, heating the mixture in an oil bath to 80° C., when superheated steam at 110° C. was introduced. The temperature of the mass quickly reached 130° C., with the simultaneous formation of a turbid solution and practically complete decomposition of the sulfonic acids. The liberated cresols could either be distilled over with steam or recovered at once by extraction. The decomposition of the salt was completed by increasing the temperature to 145° C.

The mother liquor was further evaporated for a second crop and the crystal treated as above. The cresols from the final mother liquor were also recovered in a similar manner.

The recovered nonsulfonated cresols amounted to 66.7 per cent of the crude product and contained 44.8 per cent *m*-cresol and, by difference, 55.2 per cent *p*-cresol. A method for the separation of *p*-cresol from this material is described below.

In the following summary the yields are calculated on the assumption that the liquor from the pressing of the first crop of crystal would be recovered and added to the main mother liquor previous to evaporation for the second crop, and the liquor from the second crop added to the final residual mother liquor.

	First Crop	Second Crop	Mother Liquor
Sp. gr. of liquor, 60° C.	1.190	1.205	....
Vol. of filtrate, 15° C., cc.	264	169	....
Sp. gr. of filtrate at 15° C.	1.175	1.190	....
Weight of pressed crystal, grams	119	45	..
Weight of cresols, grams	50.6	22.5	54.8
Per cent *m*-cresol in product	97.7	87.5	77.2

The corresponding product obtained without previous removal of the adhering mother liquor by pressing had a *m*-cresol content of 92.4 per cent.

Thus a product containing 97.7 per cent *m*-cresol may be obtained by the fractional crystallization of the ammonium salts of a mixture of the monosulfonic acids of *m*- and *p*-cresol prepared as above.

Para-Cresol

A comparatively pure *p*-cresol may be isolated from the crude 59 to 60 per cent *m*-cresol product in either one or two stages of preferential sulfonation, according to whether the separation is considered for *p*-cresol alone or includes the isolation of the two isomers simultaneously.

In a one-stage sulfonation an 88 to 90 per cent *p*-cresol may readily be obtained by treating the crude 59.4 per cent *m*-cresol with its own weight of 96 per cent sulfuric acid at 40° C. for 6 hrs. and purification of the recovered nonsulfonated cresols as described later. Under these conditions, however, the excessive amount of sulfuric acid requisite to give the high percentage para yields a correspondingly large amount of sulfonate with a percentage composition of approximately 68 per cent *m*- and, by difference, 32 per cent *p*-cresol. This is a very unsatisfactory intermediate sulfonate. It is not immediately adaptable for the separation of a pure *m*-cresol and would yield only an approximate 85 per cent meta product by the crystallization of the ammonium salts. Nor is the 68 per cent *m*-cresol a suitable final product as recovered, without further purification, from the sulfonate.

It is preferable to consider the separation of *p*-cresol in conjunction with the method already described for pure *m*-cresol and to isolate the former in two stages of preferential sulfonation according to the following scheme.

The first-stage sulfonation of the 59 to 60 per cent crude *m*-cresol gives two intermediate products: (*a*) an extract of nonsulfonated cresols which is the basis for the subsequent separation of a high percentage *p*-cresol, and (*b*) the first sulfonate with a percentage meta content of 78 to 80 per cent, suitable for immediate conversion into the ammonium salts and crystallization of the latter to yield a pure *m*-cresol. By the re-sulfonation of the nonsulfonated cresols (*a*) with the requisite quantity of concentrated sulfuric acid, two further products are obtained: (*c*) a second extract of nonsulfonated cresols with a high percentage para, equivalent in composition to the above one-stage sulfonation product, and yields on removal of the hydrocarbons, freezing and draining of the residual product, an 88 to 90 per cent *p*-cresol, and (*d*) a second sulfonate with a percentage composition approximately equivalent to the original crude meta-para product. The cresols from this second sulfonate, with the additional advantage of being free of hydrocarbons, may be returned to the crude 59 to 60 per cent meta product and used in a second cycle of operations..

The separation of the two isomers by this method is illustrated by the following experiment.

One hundred grams of the 59.4 per cent *m*-cresol product were sulfonated with 50 g. of 96 per cent sulfuric acid at 40° C. for 6 hrs. The sulfonation mass was poured into 150 cc. of water and the nonsulfonated cresols recovered in the usual manner. The extract (*a*) of 61.4 g. had the percentage composition of 40.4 per cent *m*-cresol, 2.1 per cent hydrocarbons and, by difference, 36.5 per cent *p*-cresol.

Decomposition of the aqueous solution of the sulfonated cresols yielded 37.7 g. with an analysis of 78.5 per cent *m*-, and, by difference, 21.5 per cent *p*-cresol. Thus the first sulfonate (*b*) has a similar composition to that obtained in the previous section and may be immediately converted into the ammonium salts of the sulfonic acids for a final separation of a 98 to 100 per cent *m*-cresol.

The first extract (*a*) of nonsulfonated cresols has now to be re-sulfonated with such a quantity of acid as will give a second extract (*c*) of a high percentage *p*-cresol and a second sulfonate (*d*) with a percentage composition equivalent to the original crude material.

For this purpose the 61.4 g. were sulfonated with their own weight of 96 per cent sulfuric acid under the usual conditions, and the nonsulfonated and sulfonated products recovered as hitherto.

The second sulfonate (*d*) yielded 46.4 g., with an analysis of 58.5 per cent *m*-cresol and, by difference, 41.5 per cent *p*-cresol. The yields of these products on the crude 59 to 60 per cent *m*-cresol are approximately equivalent to 46 and 47 per cent of the *m*- and *p*-cresol, respectively. The percentage composition of the second sulfonate is therefore almost identical with that of the original crude *meta-para* product.

The second extract (*c*) of nonsulfonated cresols yielded 13.1 g., consisting of 9.8 per cent *m*-cresol, 9.9 per cent hydrocarbons and, by difference, 80.3 per cent *p*-cresol.

This product may be further purified by addition of an excess of caustic soda, removal of the hydrocarbons with steam, and recovery of the cresols from the sodium cresylate in the usual manner. By freezing and draining the residual crystalline product under vacuo, a product may finally be obtained with a *m*-cresol content of 6 to 7 per cent and a crystallization point of 22.7° C., equivalent to approximately 89 per cent *p*-cresol.

The *p*-cresol was estimated by the determination of the freezing point and the corresponding percentage was read from a previously prepared graph obtained by plotting the freezing point of known mixtures, with a maximum impurity of 30 per cent *m*-cresol in order to be well above the eutectic point, of specially purified *m*- and *p*-cresols.

It was found that the freezing point of *p*-cresol was depressed to almost exactly the same extent by equal weights of either *o*- or *m*-cresols, and the two freezing-point curves were almost identical. This has since been confirmed by the more exhaustive work on the freezing points of known mixtures of phenol and the three cresols by Dawson and Mountford.[6]

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[6] *J. Chem. Soc.*, **113** (1918), 923.

The Training of the Industrial Chemist[1]

By George Warren Walker

HUPP MOTOR CAR CORPORATION, DETROIT, MICHIGAN

IN any adequate consideration of the training of the industrial chemist, two things must be kept in view: first, what are the conditions requisite for the best training or education of the individual? and second, what are the conditions in industry for which that individual is to be fitted?

The latter will be considered first. What are the industrial conditions and the demands of industry? Whatever other purposes and demands may be put forward from time to time, it must be kept in mind that, in the United States at least, the primary and fundamental purpose of industry is to *produce a profit*, either immediately or without any considerable delay. General managers and stockholders do not look kindly upon any proposed investigation which does not promise, with some degree of certainty, adequate profits in the near future. Any investigation, however sound theoretically, which would involve considerable cost and a somewhat prolonged period of time for its completion, would receive scant attention, especially if the question of profit was at all uncertain.

In the main, then, industry is confined to fairly well-established lines of business in which the profits are fairly certain, that is to say, lines of business in which the investigation of new processes and products is given little or no consideration as the main lines of development work have been completed.

Of course, here and there a firm or an individual may be doing considerable work in developing new products and processes as a result of exceptionable management or conditions. But these exceptions only serve to emphasize the conservative character of industry as a whole.

In industry conducted for a profit it follows that, of necessity, a large part of the work has been reduced to a routine, mechanical, chemical, etc. This at once facilitates the calculation of gains and losses, and renders more certain the adequate control of profits.

From time to time, a new process or a new product is brought out by some struggling concern or individual. The improvement may be of such a novel or revolutionary character that established lines of industry are compelled to readjust themselves. Such changes are generally the exception. Most changes are made slowly and in minor details and extend over considerable periods of time so as not to disrupt the business and interfere with profits.

An industrial chemist on entering the factory will find that the majority of the work is of a routine character. Industries of considerable size and supposedly founded on the results of chemical investigation often do little or no work in the development of new products and processes. The management is satisfied with profits and the public is apparently satisfied with the product. To improve the product means a decrease in profits in the case where more costly processes are involved; so why change?

The industrial chemist as a general thing devotes a large part, if not all, of his time to routine work. The examination of the raw material which comes into the factory, the testing of the products turned out, some supervision of the processes of manufacture by way of addition tests cover about all that is expected of him. He is occasionally called upon to exercise some originality when a routine process breaks down or fails to function properly. On this occasion, if on no other, the management is desirous of knowing why it happened.

In view of the above, what are the conditions requisite for the best training or education of the individual chemist? The first and most important thing is to *forget all about industry*. Too many universities and colleges have endeavored to convert their laboratories into small factories to the advantage of neither students nor industries.

The purpose of an institution of learning is to instruct and not to train factory hands. A student who intends to make a life-work of chemistry should study it from the standpoint of a scientist rather than from the standpoint of a factory manager. About the saddest spectacle a person can view is that of a university laboratory fitted out on the factory plan. No university laboratory can present the conditions found in a factory, and if it did succeed in duplicating the conditions it would cease to be a place of learning and become a factory. The purpose of the university is to instruct; the purpose of the factory is to produce a profit, and these purposes are distinct and not complementary.

The industrial chemist should have a thorough training in mathematics, physics, and chemistry as the three fundamental branches of his course. The training in mathematics should include calculus, differential equations, Fourier's theorem, etc.—a course sufficiently thorough and extensive so that the student can read with understanding and appreciation the advanced works on physical chemistry which should be included in his course. In addition to the above, a course or two in philosophy and a language, preferably German, could be included with profit. With such a training a student should go into a factory and "work up." He would have few things to unlearn. He would approach industrial problems with a fresh mind and insight, not distorted by a knowledge obtained from industrial courses which did not correspond to actual conditions.

Approaching industry with a trained mind, acquiring industrial knowledge under industrial conditions, a student will advance not only with greater satisfaction to himself but with greater profit to industry.

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[1] Received May 11, 1922.

SCIENTIFIC SOCIETIES

Report on Standardization of Sizes and Shapes of Apparatus—II

By W. D. Collins

Chairman, Committee on Guaranteed Reagents and Standard Apparatus

(Concluded)

Gas Analysis Apparatus

Recommendations in regard to gas analysis apparatus are with reference to a general stock. Several discontinued items will be carried in stock by one or two manufacturers or dealers who have a special demand for these articles or special skill in producing them.

(R) Gas pipet, Hempel, simple absorption, mounted on iron support.
(R) Same, Hempel, simple absorption, for liquid reagents only, mounted on iron support.
(R) Same, Hempel, double absorption, for solid and liquid reagents, mounted on support.
(R) Same, Hempel double absorption, for liquid reagents, mounted on iron support.
(R) Same, Hempel, simple absorption for ethylene, with glass beads, mounted on support.
(R) Same, Hempel, simple explosion, with glass stopcock and platinum electrodes, mounted on iron support.
(R) Same, Hempel, explosion, with stopcock, platinum electrodes, sepaate leveling bulb and connecting tube, mounted on iron support.
(D) Same, Hempel, explosion, tall form with electrodes for producing oxygen and hydrogen, mounted on iron support.
(D) Same, Hempel, double, for preparation of pure hydrogen.
(R) Same, United Gas Improvement Company form, double, for cuprous chloride, mounted on iron support.
(R) Same, Winkler, for the determination of CH_4 with removable platinum spiral, mounted on a metal support.
(R) Platinum spiral only, mounted in a double glass tube.
(R) Orsat-Muencke, apparatus for the analysis of CO_2 and O_2 especially adapted for furnace and flue gases.
(D) Orsat-Fisher, apparatus designed for portability.
(R) Orsat-Lunge, apparatus with four pipets and bent palladium tube with lamp, for separate estimation of hydrogen.
(R) Petterson-Palmquist, apparatus for determining small quantities of CO_2 in air.
(D) Portable Orsat, very light form for the determination of CO_2, CO, and O_2.
(D) Same, with only two absorption bulbs, for CO_2 and O_2.
(D) Same, with four absorption bulbs, for CO_2, CO, O_2, and H_2.
(D) Portable boiler tester, for determining the draft and percentage of CO_2 in flue.
(D) Apparatus, U. S. Steel Corporation.
(R) Apparatus, Williams Improved, Model A, for complete analysis of combustible gases.
(R) Apparatus, Williams Improved, Model B, with three bubbling pipets for determining CO_2, CO, and O_2.
(D) Chancel, apparatus for determining the specific gravity of gases.
(D) Gas apparatus, Elliott, improved form, for sulfur, as described in Technologic Paper No. 20 of the U. S. Bureau of Standards.
(D) Gas apparatus, Hinman-Jenkins, for sulfur.
(R) Gas apparatus, Referees, for S.
(D) [illegible]
(D) Apparatus analysis of mine air, laboratory form.
(D) Apparatus for determination of CH_4 in mine air, portable form.
(D) Apparatus for determination of CO_2 and CH_4, portable form.
(D) Apparatus for the determination of CO_2 and CH_4, laboratory form.
(D) Modified Orsat gas analysis apparatus, portable form, for analyzing mine gases to an accuracy of 0.2 per cent.
(R) For the analysis of gas mixtures containing CO_2, C_2H_4, O_2, CO, H_2, [illegible] **42**, p. 13, [illegible]
(D) [illegible] of copper oxide or [illegible] 42, [illegible]
(D) For analyzing natural gas, laboratory form.
(D) Gas analysis apparatus, Burrell, for determining benzene or gasoline vapor in gas mixtures by the freezing method.
(R) Gas buret, Bunte, with two stopcocks, without water jacket.
(R) Same, with water jacket fitted with rubber stoppers.
(R) Same, Hempel without stopcocks on metal base. (D) On wooden base.
(R) Same, Hempel-Winkler, with graduated buret provided with two stopcocks. (D) On wooden base.
(R) Same, Hempel, with compensating tube.
(R) Same, Hempel-Tutweiler, with 4-way stopcock, compensating tube, etc.

Gas collecting tubes, of glass, long form, with two glass stopcocks:

Sizes, cc.	125	250	500
	D	R	D

(D) Same, short form, of glass with two stopcocks, capacity 125 cc.
(R) Same, Illinois Steel Company of glass without stopcocks.
(R) Same, rubber, double acting, for use in filling tubes and bottles.
(R) Same, Winkler, of zinc with two brass stopcocks.
(R) Same, U. S. Bureau of Mines form, of glass, with two stopcocks.
(D) Gas collector, Doremus, for collecting gases from canned goods for analysis.

Gas generating bottles, without fittings:

Capacity, cc.	250	500	1000	2000
	R	R	R	D

Gas generating bottles, fitted with rubber stopper funnel tube and delivery tube:

Capacity, cc.	250	500	1000	2000
	R	R	R	D

(D) Gas generator, Hinds, for H_2S and other gases; intended for individual use.
(D) Same, dropping, Freas.
(R) Balloons, glass, very thin for weighing gases, capacity about 250 cc. With one tube and stopcock. (R) With two tubes and stopcock. (D) With one or two tubes without stopcocks
(R) Same, Dumas type, capacity about 200 cc.
(D) Gas measuring tube, Kahlenberg.
(D) Burner, Carpenter's Metropolitan Argand No. 2.
(D) Edgerton standard screen, for Argand burner.
(D) Candle balance.
(D) Cubic foot bottle, immersion form.
(D) Same, cabinet form.
(D) Same, capacity $^1/_{10}$ cu. ft. or $^1/_{12}$ cu. ft.
(D) Gas pipet, Hempel, modified by Morgan.
(D) Same, modified by Gill, for C_2H_4.
(D) Same, Gill, explosion, of very heavy glass.
(D) Same, Hempel, for determining O_2 by the exact method.
(D) Gas apparatus, Orsat-Muencke, Petrizilka modification.
(D) Same, Orsat-Tuttle.
(D) Same, Elliott, 3-way stopcock for drawing in gases; complete with explosion buret.
(R) Same, Elliott-Uhlig.
(D) Lindemann—Winkler, apparatus for determining oxygen in gaseous mixtures.
(D) Apparatus for testing oxygen.
(D) Winkler, apparatus for small quantities of CO_2.
(R) Haldane, apparatus for analysis of mine gases.
(R) Haldane, portable apparatus; for small quantities of CO_2 in air.
(D) Portable apparatus, for accurate determination of CO_2 and CH_4 in mine air.
(D) Portable apparatus, for exact determination of CO_2 and O_2.
(D) For CO_2 only.
(D) Gas apparatus, Burrell-Oberfell, laboratory type, complete on 3 stands.
(D) Gas apparatus, for CO_2 in alveolar air and blood.
(D) Gas apparatus, Haldane, modified by Henderson.
(D) Same, Ruedorff, for determination of CO_2 or moisture.
(R) Same, Tutweiler, for determination of H_2S in illuminating and other gases.
(D) Same, Elliott, latest form, for determination of sulfur.
(D) Same, Graefe, for determination of sulfur.
(D) Same, E & A, for determination of sulfur and halogens in oils.
(D) Same, Drehschmidt, for sulfur in gas.
(D) Same, Reich, for SO_2 in lead chambers.
(D) Same, Cooper-Chollar.
(D) Gas buret, Winkler, complete with support.
(D) Gas buret, White, for exact gas analysis.
(D) Harcourt pentane lamp.

(D) Gas filter of glass, with purified filter paper cup.
(D) Gas filter, with ground-in connection.
(R) Gas distributor of brass, with connections for 3 burners and one gas pipe; with stopcocks. (D) Without stopcocks. (D) With 3 stopcocks and center light.

Gas holder, of heavy zinc, with water gage:

Capacity, gal.	5	10
	D	D

Same, of heavy copper:

Capacity, gal.	5	10
	R	R

(D) Same, with sliding receiver, made of leaded iron.

Tube, gas measuring, Bunsen:

Capacity, cc.	25	50	50	100	200
Graduated to cc.	$^1/_{10}$	$^1/_5$	$^1/_{10}$	$^1/_5$	$^1/_{10}$
	D	D	R	R	D

Same, with stopcock:

Capacity, cc.	50	100	100
Graduated to cc.	$^1/_{10}$	$^1/_5$	$^1/_{10}$
	R	D	D

(D) Tube, Kemp, capacity 100 cc. or 175 cc.
(D) Tube, gas washing, Kjeldahl.
(D) Same, Muencke, with or without stopcock.
(D) Same, Vogel.

Gas Generator

Automatic. Bell glass in heavy glass jar, brass stopcock:

Height, in.	8	12	20
	D	D	D

Heumann:

Capacity, liters	2	4	8
	D	D	D

(D) Babo.
(D) Hinds for H_2S.

Kipp, small base:

Capacity, cc.	250	500	1000	2000	4000
	D	D	D	D	D

Kipp, with broad base:

Capacity, cc.	250	500	1000	2000	4000
	D	R	R	R	D

(D) Munn.
(R) For generating O_2 from "O."
(R) Parsons.

Stoneware for Cl and other gases:

Capacity, gal.	$6^1/_2$	13	20	$26^1/_2$	33	40
	D	D	D	D	D	D

Stoneware with round bottom:

Capacity, gal.	$^1/_8$	$^1/_4$	$^1/_2$	1	$1^1/_2$
	D	D	D	D	D

Gasoline gas, cylindrical:

Sizes:	Small	Large
	D	D

Gasoline gas, rectangular:

Capacity about	$^1/_4$ gal.	$1^1/_2$ gal.
	D	D

Pipets

(D) Automatic, dropping, with rubber bulb, for delivering exactly 1 cc.

Automatic, overflow, with patent 3-way stopcock; reservoir for collecting the excess; ground connections:

Sizes, cc.	10	25	50	100
	D	D	D	D

(D) Same, with capacity of 17.6 cc. for milk testing.

Same, with rubber connections:

Sizes, cc.	10	25	50	100
	R	R	R	D

Calibrating, Ostwald's; capacity 2 cc.:

Sizes, cc.	1	2	5
	D	R	R

(R) Capillary, for preparing milk smears on microscope slides for counting the bacteria present. Graduated at $^1/_{100}$ cc.
(R) Dropping, medicine droppers, with rubber bulb, length 4 in. Tip straight or curved.
(D) Mercury, for handling small drops of mercury.

Mohr, accurately graduated in cc. and fractions with glass stopcock:

Sizes, cc.	25	50
	D	D

To deliver, Ostwald, as used in the determination of nitrogen, urea, and ammonia in urine by the Folin method:

Sizes, cc.	1	2	3	5	10
	R	R	R	R	R

Without bulb, as used in bacteriological work and water analysis:

Sizes, cc.	1	5	10
	R	R	R

(R) Wassermann safety, for bacteriological work and serological work.

Water analysis, as used in the Hygienic Laboratory of the U. S. Public Health Service:

Sizes, cc.	2	10	11
	R	R	R

Siphon, Struthers:

Sizes, cc.	25	50
	D	D

Straight, drawn to a point:

Length, in.	6	7	8	10	12	15	18
	D	D	R	D	R	D	D

Same as above with rubber bulb of 25-cc. capacity:

Length, in.	6	7	8	10	12	15	18
	D	D	R	D	R	D	D

Ungraduated, with bulb:

Capacity, cc.	1	2	5	10	25	50	100	200
	D	D	D	D	D	D	D	D

Volumetric, accurately graduated:

Capacity, cc.	1	2	3	4	5	10	$12^1/_2$	15	20	25	30
	R	R	D	D	R	R	D	D	R	R	D

	50	75	100	200
	R	D	R	R

Volumetric, short form, accurately graduated:

Capacity, cc.	1	2	5	10	20	25	50	100	200
	D	D	R	R	D	R	D	D	D

Mohr, accurately graduated in cc. and fractions:

Capacity, cc.	$^2/_{10}$	$^1/_{10}$	1	1	2	2	2	5	5	5
Subdivisions, cc.	$^1/_{100}$	$^1/_{100}$	$^1/_{100}$	$^1/_{10}$	$^1/_{50}$	$^1/_{10}$	$^1/_{20}$	$^1/_{100}$	$^1/_{20}$	$^1/_{10}$
	D	R	R	R	D	R	D	D	R	R

	10	10	20	25	50	50	100	100
	$^1/_{10}$	$^1/_{20}$	$^1/_{10}$	$^1/_{10}$	$^1/_{10}$	$^1/_5$	$^1/_5$	$^1/_{10}$
	R	D	D	R	D	D	D	D

Mohr, graduated to tip, serological:

Capacity, cc.	$^1/_{10}$	$^2/_{10}$	1	1	2	2	5	5	25	50
Subdivisions, cc.	$^1/_{100}$	$^1/_{100}$	$^1/_{100}$	$^1/_{10}$	$^1/_{10}$	$^1/_{20}$	$^1/_{10}$	$^1/_{20}$	$^1/_{10}$	[illegible]
	R	R	R	R	R	D	R	D	D	D

	50	100	10	10
	$^1/_{10}$	$^1/_{10}$	$^1/_{10}$	$^1/_{20}$
	D	D	R	D

Automatic, Bailey, with stand:

Graduated capacity, cc.	10	25	50	100
	D	D	D	D

Automatic, Bleckman, with reservoir, iron stand and spring clamp:

Capacity, cc.	5	10	25
	D	D	D

Automatic, G & F:

Capacity, cc.	10	25	50	100
	D	D	D	D

(D) Automatic, LeDocte.
(D) Donnan, to show emulsifying power of a liquid.
(R) Mercury, for taking up mercury without danger.
(D) Overflow, Rickett, for silver assay.
(D) Rothe

Safety, for acids and poisonous liquids:

Capacity, cc.	2	5	10	25	50	100
	D	D	D	D	D	D

Bottle, with a capped pipet ground into neck; for volatile liquids:

With pipet, cc	10	25	50	100
	D	D	D	D

(R) Glucose, Spencer, capacity 50 cc., graduated, 5°–20° Brix, in $^1/_5$°
Sucrose, capacity 52.096 cc., graduated 5°–25° Brix, in $^1/_{10}$°.

Rubber Tubing

Recommendations in regard to rubber tubing are made with reference to color in the understanding that mere color is of no significance as to quality. It seems to be agreed that only two grades of tubing are needed, a "compound" tubing and a so-called "pure gum." These differ in rubber content and in flexibility. The "pure gum" usually contains more rubber than the "compound" and is more flexible. The "pure gum" has generally been black, although some red tubing has been of this grade. "Compound" tubing has been white, red, gray, or black. Several large dealers have discontinued the red tubing without experiencing difficulty in satisfying the needs of their customers. The Committee has left out the red, has taken white to represent compound tubing and black for pure gum, and has recommended sizes that are now in use.

White, light wall:

Inside diam., in.	1/8	3/16	1/4	5/16	3/8	1/2	5/8	3/4	1
Wall thickness, in.	[illegible]	3/64	1/16	1/16	1/16	1/16			
	R	R	R	R	R	R	D	D	D

White, heavy wall:

Inside diam., in.	1/8	3/16	1/4	5/16	3/8	1/2	5/8	3/4	1
Wall thickness, in.	3/32	3/32	1/8	1/8	1/8	1/8	1/8	1/8	1/8
	R	R	R	R	R	R	R	R	R

Light wall, black, pure unvulcanized gum:

Inside diam., in.	1/8	5/32	3/16	1/4	5/16	3/8	1/2	5/8	3/4	1
Wall thickness, in.	1/32		3/64	1/16	1/16	1/16	3/32			
	R	D	R	R	R	R	R	D	D	D

Heavy wall, black, pure unvulcanized gum:

Inside diam., in.	1/8	5/32	3/16	1/4	5/16	3/8	1/2	5/8	3/4	1
Wall thickness, in.	1/16		3/32	3/32	3/32	1/8	1/8	1/8	1/8	1/8
	R	D	R	R	R	R	R	R	R	R

Heavy wall, black, a less expensive quality:

Inside diam., in.	1/8	5/32	3/16	1/4	5/16	3/8	1/2
	D	D	D	D	D	D	D

Light wall, red:

Inside diam., in.	1/8	5/32	3/16	1/4	5/16	3/8	1/2	5/8	1	3/4
	D	D	D	D	D	D	D	D	D	D

Heavy wall, red:

Inside diam., in.	1/8	5/32	3/16	1/4	5/16	3/8	1/2
	D	D	D	D	D	D	D

5/8	3/4	1
D	D	D

Heavy wall, red, a less expensive quality:

Inside diam., in.	1/8	5/32	3/16	1/4	5/16	3/8	1/2
	D	D	D	D	D	D	D

[illegible] flat wall

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]

[illegible] vacuum pump connections:

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	3/8	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]		1/4
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

Pressure, with canvas insertion, for vacuum connections:

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]		[illegible]	[illegible]			
	[illegible]	[illegible]	[illegible]	D	[illegible]	[illegible]

Stopcocks

[illegible]

Brass, both ends for tubing connections.

Bore, in.	1/8	1/4
	R	R

Brass, with male or female screw and tubing attachment:

Bore, in.	1/8	1/4
	R	R

Brass, with male or female screw at both ends:

Bore, in.	1/8	1/4
	R	R

Brass, with male and female screw:

Bore, in.	1/8	1/4
	R	R

(D) Brass, for gas, male and female screw, and tubing attachment.

Brass, for gas, with quadrant and pointer to regulate the gas supply:

Bore, in.	3/8	1/2
	D	D

(D) Hard rubber, each end for rubber connection.

Nipples, of brass, with male or female thread:

Bore, in.	1/8	1/4
	R	R

Glass, for attaching to buret:

Bore, mm.	2
	R

Geissler:

Bore of stopper, mm.	1	2	3	4	5	6	8	10
	R	R	R	R	R	R	R	R

(R) With capillary tube 6 to 7 mm. for gas analysis connections, etc., 1 1/2 mm. bore.

Geissler, bent, for aspirator bottles, etc.:

Bore of stopper, mm.	1	2	3	4	5	10
	D	R	R	R	D	D

With oblique bored stopper:

Bore of stopper, mm.	2	4
	R	R

(R) With oblique bored stopper, with capillary tube, 1 1/2 mm. bore.

Three-way:

Bore of stopper, mm.	1	2	4
	D	R	R

(R) Three-way, with capillary tube, 1 1/2 mm. bore.

Three-way, with downward inlet, with plug bored at angle:

Bore of stopper, mm.	2	4
	R	R

(R) Same, with capillary tube, 1 1/2 mm. bore.

Geissler, three-way:

Bore of stopper, mm.	1	2	4
	D	R	R

(R) Same, with capillary tube, 1 1/2 mm. bore.

With downward inlet:

Bore of stopper, mm.	1	2	4
	D	R	R

(R) Same, with capillary tube, 1 1/2 mm. bore.

With downward inlet and with rubber connection below stopper:

Bore of stopper, mm.	2	4
	D	D

Four-way:

Bore of stopper, mm.	2	4
Heavy glass, with bib:	R	R

Bore of stopper, mm.	3	5	8	10
	D	D	D	D

Stoneware:

Bore of stopper, in.	3/8	1/2	3/4	1	1 1/4	1 1/2
	D	D	D	D	D	D

Stoneware, with two male threads:

Bore of stopper, in.	3/4	1/2	3/4	1	1 1/4	1 1/2
	D	D	D	D	D	D

2	2 1/2	3
D	D	D

Stoneware, with one male thread and bulb:

Bore of stopper, in.	3/8	1/2	3/4	1	1 1/4	1 1/2
	D	D	D	D	D	D

2	2 1/2	3
D	D	D

Glass, two-way, with mercury seal, and plug bored at an angle:

Bore of stopper, mm.	2	4
	D	D

(R) Glass, Fresenius form, for buret tips. With inlet tube bore, 5 mm.; outlet bore, 2 mm.

Special Bottles

Volatile liquid, glass stoppered with ground-on glass cap:

250 cc.	500 cc.
R	R

(R) Balsam, wide mouth, with glass rod and glass cap ground to fit against shoulder of bottle, 45 cc.
(R) Immersion, oil, with nickel-plated cap and device for regulating amount of oil on plunger
(D) Immersion, oil, with wooden stopper and wire dropper.
(D) Specific gravity, Weld.

Aspirator, of heavy glass, with large tubulature at bottom for stopper:

Liters:	$^1/_8$	$^1/_4$	$^1/_2$	1	2	4	8	12	20	32
	D	R	R	R	R	R	R	R	R	D

Aspirator, of heavy glass, with stopper and glass stopcock ground in outlet:

Liters:	$^1/_4$	$^1/_2$	1	2	4	8	12	20	32
	D	R	R	R	R	R	R	R	D

Aspirator, heavy glass, with narrow outlet for connecting rubber tubing:

Liter:	$^1/_8$	$^1/_4$	$^1/_2$	1	2	4	8
	R	R	R	R	R	R	R

Balsam, with glass rod, glass cap ground to fit outside of neck:

Cc.	30	60
	R	D

Ceresin wax, for hydrofluoric acid:

Cc.	30	150	250	500
	D	D	D	D

(R) Dropping, square, with rubber pipet stopper, 30 cc.

Dropping, with ground-in pipet, and rubber nipple:

Cc.	15	30	60
	D	R	R

Dropping, with ball top pipet ground in:

Cc.	15	30	60
	D	D	D

Dropping, low form, with ball top pipet ground in:

Cc.	30	60
	D	D

Dropping, with thistle top pipet ground in:

Cc.	30	60
	D	D

Acid dropping, tall form, with long ground-in stopper and ground cap:

Cc.	30	60
	D	D

Same, low form:

Cc.	30	60
	R	R

Bottle, dropping, "TK" with grooved flat stopper white glass:

Cc.	15	30	50	100	200
	R	R	R	R	R

Same, amber glass:

Cc.	15	30	50	100	200
	D	R	R	R	D

Dropping with grooved high stopper:

Cc.	15	30	50	100
	R	R	R	R

Dropping, Shuster with glass stopper:

Cc.	30	60
	R	D

Same, without stopper:

Cc.	30	60
	R	D

(D) Dropping, Salleron, 30 cc.

Gas washing, Allihn, double action with ground-in stopper:

Cc.	250	500	1000	2000
	R	R	R	D

Gas washing, Allihn, with valve to prevent liquid flowing back:

Cc.	250	500	1000
	D	D	D

Gas washing, Sillimann, fitted with rubber stopper:

Cc.	250	500
	D	D

Gas washing, Cloez:

Cc.	125	250	500	1000
	D	D	D	D

Gas washing, Drechsel, low form, with ground-in stopper:

Cc.	125	250	350	500	1000
	R	R	D	R	D

Gas washing, Drechsel, tall form, with ground-in stopper

Cc.	125	250	350	500	1000
	R	R	D	R	D

(R) Gas washing, Friedrich.

Gas washing, improved, for either solids or liquids:

Cc.	250	500	1000
	D	D	D

(D) Gas washing, Habermann.
(D) Gas washing, Muencke.
(D) Gas washing, Raibow.

Lead, for hydrofluoric acid, stoppered:

Oz.	4	8	16	32
	D	D	D	D

(D) Oil immersion, with glass rod and ground cap; 20 cc.
(R) Oil immersion, Mach, improved form with loose fitting metal cap and dropper; 30 cc.

Oil sample, long form:

Oz.	1	2	4	8
	D	R	R	R

(R) Same, with polished bottom; 4 oz.

Pressure, pear shaped, round bottom, with patent stopper:

Cc.	60	100	200
	D	D	R

(D) Pressure, E & A same shape as above but heavier with grooved glass stopper to tie over; 250 cc.
(D) Pressure, Saloman; 125 cc.

Pressure, Lintner:

Cc.	125	250
	R	D

Bottle, specific gravity, unadjusted, with perforated stopper:

Cc.	1	2	5	10	25	50	100
	D	D	R	R	R	R	D

Same, accurately adjusted:

Cc.	1	2	5	10	25	50	100
	D	D	R	R	R	R	R

Same, in paper box with tare weight:

Cc.	10	25	50	100
	D	R	R	D

Specific gravity, boot, Morgan modification, double wall with vacuum:

Cc.	10	25	50	100
	R	R	R	D

Specific gravity, with ground-in centigrade thermometer, divided in $^1/_5$° and stoppered capillary tube:

Cc.	10	25	50	100
	D	R	R	R

Specific gravity, Squibb, for liquids:

Cc.	25	50	100
	D	D	D

(R) Specific gravity, Walker, for very fluid liquids.
(R) Specific gravity, Walker, for very viscous liquids.
(D) Weighing, Hill, about 30 cc.

Specific gravity, Regnault, for liquids:

Cc.	25	50
	D	D

Specific gravity, with stopper, ground to fit:

Cc.	25	50
	D	D

(R) Specific gravity, Sprengel, with ground-in suction tube.
(D) Specific gravity, Sprengel, with thermometer and ground-in suction tube.
(R) Specific gravity, Nicholl tube, for liquids.

Specific gravity, according to Hulett, similar to a Sprengel bottle, but made so as to stand on the balance:

Cc.	25	50
	D	D

Specific gravity, Regnault, for solids:

Cc.	25	50
	D	R

(R) Specific gravity, Hogarth, for iron ores.
(R) Specific gravity, Hubbard, for semisolid bitumens.
(R) Specific gravity, Hubbard, modified, for semisolid bitumens.
(D) Specific gravity, Thoerner volumeter, for solids, especially coke and charcoal, etc.

[illegible]

Cc.	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]

[illegible]

[illegible] stoneware bib stopcock ground in the outlet. Capacity 100 liters.

Washing, ring neck flask, fitted with rubber stopper and movable exit tube:

Cc.	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	2000
	D	[illegible]	R	D	R	D

Same, fitted with handle:

Cc.	[illegible]	[illegible]	[illegible]	750	1000	2000
	[illegible]	D	D	D	D	D

With wicker covered neck, for hot water; including rubber stopper and glass tubes:

Cc.	[illegible]	1000
	R	R

Washing, Griffin, continuous flow:

Cc.	[illegible]	[illegible]	[illegible]	750	1000
	D	D	D	D	D

(D) The tube only for above.

Washing, with safety mouthpiece:

Cc.	250	500	1000
	D	D	D

(D) Washing, with rubber bulb, with air valve.

Washing, with tubulated glass stopper, ground into the neck:

Cc.	250	500	1000
	R	R	R

Washing, with tubulated glass stopper, ground in, and tubes each fitted with glass stopcock

Cc.	250	500	1000
	R	D	D

Woulff, heavy glass with 2 necks:

Cc.	125	250	500	750	1000	2000	4000	8000
	R	R	R	D	R	R	R	R

Same, with 3 necks.

Cc.	125	250	500	750	1000	2000	4000	8000
	R	R	R	D	R	R	R	R

Woulff, with 2 necks and outlet at bottom:

Cc.	250	500	1000	2000	4000	8000
	R	R	R	R	R	D

Same, with 3 necks:

Cc.	250	500	1000	2000	4000	8000
	R	R	R	R	R	D

Woulff with 3 necks, center one stoppered, delivery tubes ground into the other necks

Cc	125	250	500	1000
	D	D	D	D

(R) Weighing.[1] Cylindrical form, ground glass stoppers without neck:

Height, mm.	50	80	40	50	50	60	80	30	30	30
Diameter, mm.	[illegible]	[illegible]	25	25	40	30	40	50	60	70
	R	R	R	R	R	R	R	R	R	R

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[1] Previously published in This Journal, 13 (1921), 1073-4.

Calendar of Meetings

American Ceramic Society Summer Excursion Meeting, Rochester, Montreal, Ottawa, Kingston, Toronto, Hamilton, Niagara Falls, and Buffalo, August 13 to 19, 1922

American Pharmaceutical Association—70th Annual Meeting, [illegible] 14 to 20, 1922

Annual Safety Congress of the National Safety Council—Detroit, Mich., [illegible] 1922

American Chemical Society—64th Meeting, Pittsburgh, Pa., [illegible]

Eighth National Exposition of Chemical Industries—New York, N. Y., [illegible]

American Electrochemical Society—42nd Meeting, Montreal, Canada, [illegible]

American Society for Steel Treating—Convention, Detroit, Mich., [illegible]

Pittsburgh Meeting, A. C. S.

Arrangements for the September Meeting of the SOCIETY are nearly complete and the preliminary program has already been mailed to the members. The final program will be sent about August 28 to the Secretaries of Local Sections, to the Council, to members of the Pittsburgh Section, and to all other members making special request therefor.

GENERAL PROGRAM

MONDAY, SEPTEMBER 4

1:30 P. M.—Registration of Councilors and wives at Blue Room, William Penn Hotel.
2:30 P. M.—Council Meeting, at Blue Room, William Penn Hotel.
6:30 P. M.—Dinner at Duquesne Club for councilors and wives.
8:15 P. M.—Theater Party for Councilors' wives.
8:15 P. M.—Council Meeting continued or theater party.

TUESDAY, SEPTEMBER 5

9:00 A. M.—Registration and reception of members and guests at Carnegie Music Hall.
10:30 A. M.—General Meeting, Carnegie Music Hall.
Address of Welcome.
Response, Edgar F. Smith, President of the AMERICAN CHEMICAL SOCIETY.
General Addresses, including the following:
1. J. H. James. "Pittsburgh as an Industrial Center: Historical and Industrial."
2. W. F. Rittman. "Pittsburgh as an Industrial Center: Finance and Transportation."
(Complete list on final program.)
2:00 P. M.—General Meeting. Carnegie Music Hall. Special addresses will be given, of which the following are part:
1. Thos. Midgley, Jr., and T. A. Boyd. "The Chemical Control of Gaseous Detonation with Particular Reference to the Internal Combustion Engine." (Illustrated by experiments and slides.) Discussion later by Industrial Division.
2. E. J. Crane. "The Journal Literature of Chemistry."
3. Wilder D. Bancroft. "Structural Colors in Feathers."
2:00 P. M.—Ladies' trip to Country Club.
8:15 P. M.—Smoker at Syria Mosque. Special Features.
8:15 P. M.—Drama School Play for ladies, Carnegie Institute of Technology.

WEDNESDAY, SEPTEMBER 6

9:30 A. M.—Divisional and Sectional Meetings. Carnegie Institute of Technology.
10:00 A. M.—The ladies will visit the Heinz factory and lunch there.
2:00 P. M.—Divisional and Sectional Meetings. Carnegie Institute of Technology.
4:00 P. M.—There will be a musicale for the ladies at the Twentieth Century Club.
8:15 P. M.—Public Meeting, Carnegie Music Hall. Reception.

THURSDAY, SEPTEMBER 7

9:30 A. M.–2:00 P. M.—Divisional and Sectional Meetings. Carnegie Institute of Technology.
5:00 P. M.—Garden party, supper, and social evening with music and dancing at the University of Pittsburgh Faculty Club (Oak Manor), Fifth Avenue and Atwood Street.

FRIDAY, SEPTEMBER 8

Excursions to industrial plants.
Sports: Golf, tennis, baseball (amateur or professional).

SATURDAY, SEPTEMBER 9

Informal inspections, etc.

INDUSTRIAL EXCURSIONS

In the belief that the opportunity afforded to visit industrial plants constitutes one of the attractions at every meeting of the SOCIETY the following information is given regarding the Pittsburgh excursions. The final program of excursions, however, has not been completed.

On Friday, September 8, there will be an all-day excursion to plants of the American Steel and Wire Company at Donora, Pa., and of the American Window Glass Company at Monongahela City, Pa., where the following processes will be seen: zinc ore roasting; sulfuric acid manufacture (chamber process); zinc distillation; iron blast furnace practice; open-hearth steel manufacture; rolling steel into wire rods; annealing; pickling; wire drawing; galvanizing (zinc coating); recovery of ferrous sulfate from waste pickling liquors; window glass manufacture in tank furnaces and blowing of 60-ft. cylinders by the window glass machine process.

A special train will be provided for the trip, and in case 500 or more decide to go the cost of the trip, including the box lunch, will approximate $2.50. All desiring to take this trip should promptly advise Mr. L. H. Miller, Carnegie Institute of Technology, Pittsburgh, Pa., so that he may make adequate arrangements.

Mr. A. V. Bleininger will make arrangements for excursions to the ceramic plants in the neighborhood of East Liverpool, Ohio, and Newell, W. Va.

In addition to the steel works, plants of the following types will be open for inspection in the Pittsburgh district: plate glass; electrical machinery and appliances; coal mining and coke manufacturing; coke by-products; petroleum production and refining; heavy chemicals; cork products; water purification; and food manufacture and preservation.

The manufacture of steel pipe from the ore to the finished product will be shown by a moving picture film. Pittsburgh is to have a museum of industrial products and processes and some of the initial exhibits will be shown at the time of the convention.

In order that suitable arrangements may be made, members are advised to inform Mr. Earl Blough, through Mr. L. H. Miller, of the industries in which they are especially interested and the best time for them to make their visits to the plants.

It is regretted that, as a result of past experience, certain manufacturers feel that they cannot admit visitors, and in order that there may be no disappointment later we announce now that the aluminium and radium plants, as well as the research laboratory of the Westinghouse Electric and Manufacturing Co., will not be open to visiting chemists.

CHAIRMEN OF LOCAL COMMITTEES

Honorary Chairman: RICHARD B. MELLON.
Executive: JAMES O. HANDY.
Hotels and Dormitories: J. H. JAMES.
Program: A. C. FIELDNER.
Finance: E. R. WEIDLEIN.
Reception: R. E. ZIMMERMAN.
Printing and Publicity: H. H. CRAVER.
Entertainment: C. G. FISHER.
Excursions: EARL BLOUGH.
Ladies Executive: MRS. JAMES O. HANDY

National Lime Association

The Annual Convention of the National Lime Association held at Cleveland, Ohio, June 13 to 16, 1922, was devoted almost exclusively to the use of lime in the chemical industries. Since 1907 there has been a rapid and steady growth of the lime tonnage used by the chemical industries, until to-day they consume most of the lime produced. A special feature of the convention was a symposium on the technical and chemical uses of lime.

Mr. P. A. Paulson, of the Kimberly-Clarke Paper Co., discussed the milk-of-lime process for making bisulfite pulp, pointing out the many advantages in the way of quality of product and economy of operation for this process.

Mr. R. P. Shiveley, of the Monongah Glass Co., described the use of burnt lime instead of limestone in glass manufacture.

Mr. G. K. Spence, Chief Chemist, New York & Pennsylvania Paper Co., presented a paper on the use of lime in making soda and sulfate pulp, and emphasized the proposals for more effective coöperation between the lime industry and the paper industry.

The subject of centralized water-softening plants was presented by S. C. Hadden, Editor of *Municipal and County Engineering*. He pointed out that a demand for soft water is slowly but surely developing all over the country and that centralized water-softening plants are the logical solution of this problem. He further stated that there was a potential lime tonnage of about 1,000,000 a year for this use alone.

The possibilities of lime in the textile industry, particularly in connection with the boiling and bleaching of cotton goods, were set forth by Prof. Elton R. Darling, of the James Millikin University. He also mentioned the probability of lime being satisfactory for scouring wool.

Prof. F. C. Mathers, of Indiana University, gave some interesting demonstrations on the settling of lime and highly reactive quicklime. It is now possible to set out the lime sludge more rapidly than formerly, a matter of considerable importance in bleach and pulp manufacture. The highly reactive quicklime has many uses, the dehydration of alcohol and organic liquids being important. With this reactive quicklime, alcohol purer than the standard grade of absolute alcohol can be made by one-half hour's treatment, instead of the usual 24 hrs.

M. E. Holmes, Manager of the Chemical Department of the Association, reported on the activities of that department. The most important activity of the department is the research and investigational work; a comprehensive series of experiments is being carried out on the fundamental properties of quicklime, agricultural, and dehydrating lime. In addition to this research work, the department has two fellowships, one at Ohio State University, where typical limestones are being turned out under various conditions of temperature and pressure and the properties of the resulting lime determined; and the other at Indiana University for work on more specific uses of lime. The other important activity of the Chemical Department is its publicity work; during the coming year a bi-monthly publication to be known as the *Lime Digest* will probably be issued. A textbook on lime is also being prepared in coöperation with other experts.

The construction use of lime was described in papers by W. E. Emley, of the Bureau of Standards, and H. C. Berry, of the University of Pennsylvania. Mr. Emley's report dealt largely with the effect of lime on the workability and strength of concrete.

The agricultural feature of the program was a paper by Prof. W. C. O'Kane on lime in crop protection, showing especially the recent development in the use of lime for curing corn root rot. There is a potential demand for many extra tons of lime for this purpose alone.

Papers bearing on lime production were presented by Nathan C. Rockwood, of the Rock Products Co., and Irving Warner, of the Chas. Warner Co. Mr. Rockwood described the new plant of the Rockland & Rockport Corporation at Rockland, Me., which, on account of its being a marked step in advance of other lime plants, has been watched with great interest. Mr. Warner spoke from the engineering point of view about the burning of lime in rotary kilns and particularly the draft fuel inclination of the kiln, rate of discharge, etc.

The value of research to an industrial trade association was the subject of an excellent paper by E. R. Weidlein, Director of Mellon Institute; and Mr. O. B. Towne, Secetary of the Wax Paper Manufacturing Association presented the many legitimate phases of association activity and predicted an optimistic view for the future operation of this organization.

Fourteenth Semiannual Meeting of the American Institute of Chemical Engineers

In attendance, program, and interest this meeting, held at Niagara Falls, Canada, June 19 to 21, 1922, showed a great contrast to the second semiannual meeting of the American Institute of Chemical Engineers, held twelve years ago in the same room at the Hotel Clifton. At that time the membership list contained only 118 names while at this meeting the secretary reported a membership of 550, a net increase of 22 since the last meeting.

The Council reported an amendment to the Constitution providing for the organization of local sections, one of which has already been organized at Detroit, Mich.

President Henry Howard in an address at the opening session reported the following important activities since the last meeting: As a basis for coöperation with the newly organized Institution of Chemical Engineers of London, England, exchange of Transactions at cost, and the privilege of attending the meetings of each Society by members of the other Society; coöperation with Senator Stanley in drafting a working clause for the patent law by which a patentee who works his patent in a foreign country and does not manufacture in the United States must if requested give a license to an American company, the compensation to be determined at the direction of a United States District Court; to secure the establishment of American valuation in the tariff bill, and support to the Chemical Warfare Service.

The order of procedure had been changed for this meeting so that the entire morning of the first day was devoted to reading and discussion of papers. More than 100 were present at this session and this attendance was increased at subsequent sessions. The necessary business session was held on the steamer on Lake Ontario during the trip to Toronto on Tuesday, a very satisfactory arrangement.

Wednesday and Thursday mornings were devoted to the reading of papers. The entire program of papers consisted of a symposium on acid manufacture.

Sulfuric acid was first considered, the first paper being "Thermal Considerations in Sulfuric Acid Concentration," by F. C. Zeisberg. The author illustrated by curves the thermal properties of all concentrations of sulfuric acid, showing that the heat necessary to concentrate the acid from one strength to another could readily be obtained

Peter S. Gilchrist, in a paper entitled "Modern Methods of Concentrating Sulfuric Acid," described particularly a newly developed apparatus of the submerged hot air type and its application to the concentration of sludge acid from oil refining.

Dr. Ludwig A. Thiele presented a paper, with illustrations, on "Increased Capacity of Cascade Systems." This increased capacity was effected by means of a special corrugated bottom cascade basin giving increase in the effective heating surface.

L. J. Michael and James R. Withrow presented the results of a study of quartz tower packing in the glover tower. A study of a case of settling of 18 in. to 2 ft. had been made, with the result that it was shown that solubility of the quartz had not taken place but that the settling had been due to intermittent heating and cooling of the tower resulting in repacking of the quartz.

The most important paper on sulfuric acid manufacture was that by Dr. P. J. O'Gara on "Sulfur Dioxide and Fume Problems and Their Solutions." As head of the research department of the American Smelting & Refining Co., Dr. O'Gara has spent 7 yrs. at Salt Lake City, Utah, studying the effect of different concentrations of sulfur dioxide under varying conditions of light, temperature, humidity, and stage of growth, on the growth of about 200 species of plants, making the tests under field conditions. This study resulted in the discovery of "The Law of Gas Action on the Plant Cell" expressed by the fundamental equation $t(L-l) = c$, in which t is the time through which the gas acts to produce a certain effect, L is the concentration of the gas, l is the concentration of the gas which will not injure the plant, and c is a constant. The law may be stated as follows:

> With all environmental factors remaining the same, the active part of a gas necessary to produce a certain effect upon the plant cell, multiplied by the time through which it acts, is constant.

A careful study of the smoke stream was also made for the purpose of ascertaining methods by which injury to plants could be prevented by regulating the concentration of the sulfur dioxide eliminated from the stack. It was found that the temperature of the stack gases and the height of the stack were the factors to be controlled in order to prevent plant injury. Considering the topography and the environment, together with the weather factors, there is for each plant or industrial work a definite stack height and exit gas temperature necessary to insure the safety of surrounding interests.

On the manufacture of nitric acid two papers were presented. Dr. G. B. Taylor in a paper on "Some Economic Aspects of Ammonia Oxidation" gave the cost factors which determined the advisability of manufacturing nitric acid from Chile saltpeter or by oxidation of ammonia. C. D. Carpenter and J.

Barbor, in a paper on "Concentrating Dilute Nitric Acid Solutions," discussed concentration.

The problems involved in the manufacture of hydrogen and nitrogen for synthetic ammonia manufacture were pointed out by Prof. Hugh S. Taylor. He reviewed from the physical chemical standpoint all processes in use and expressed the opinion that a radical reorganization of the steam iron process from the chemical engineering and thermal standpoints might make this process a competitor of the others.

In a paper by Stephen L. Tyler on "Absorption of Hydrochloric Acid or Other Gases," he described a fused silica apparatus of new design, and Hugh K. Moore presented a paper on "Production of Hydrochloric Acid from Chlorine and Hydrogen."

The manufacture of phosphoric acid was discussed in a paper by Dr. W. H. Waggaman on "Recent Advances in the Production of Phosphoric Acid for Fertilizer and Food Purposes." The author explained the low cost of manufacture of phosphoric acid and the important advantages which would result from the substitution of phosphoric acid for sulfuric acid in fertilizer manufacture.

Several papers were read giving the progress attained in the transportation of muriatic acid and liquid chlorine. Mr. J. M. Rowland described wooden tanks lined with soft rubber, and F. C. Zeisberg told about a steel tank lined with hard rubber. A steel tank car insulated with cork board which has been in successful use for twelve years for transporting liquid chlorine was described by J. L. K. Snyder and H. P. Wells. Max Mauran described a multiple tank car for liquid chlorine consisting of a number of steel tanks of one-ton capacity carried in a steel frame on a railway truck.

Mr. Geo. T. Walker's paper on "Crystallization of Trisodium Phosphate" described the continuous crystallization of this salt

Mr. N. T. Bacon in a paper on "Vapor Tension at Low Temperatures" challenged the conclusions of Dr. Irving Langmuir with reference to the behavior of gases at temperatures and pressures so low that a sphere of six times the diameter of the earth would be necessary to accommodate a single molecule of platinum.

The program of excursions included inspection of the new power development in Ontario, Canada, of the Hydroelectric Commission. Three units of 55,000 h. p. each of the ten contemplated have already been installed.

A delightful trip was taken on Tuesday, which included the Gorge ride to Queenstown where the steamer was taken to Toronto. The party was met at Toronto by a local reception committee with automobiles, for a sight-seeing tour of the city and visits to a kodak factory, a rubber factory, and the plant of the Consumers Gas Company.

Wednesday was spent in Buffalo, where papers were read in the morning at Hotel Lafayette, and in the afternoon the party was taken by automobiles for sight-seeing and visits to Lackawanna Steel Co., Wickwire Steel Co., Buffalo General Electric Co., Steam Power Plant, Dold Packing Co., and Larkin Company. A smoker was held on Wednesday evening at Hotel Lafayette.

On Thursday afternoon plants at Niagara Falls, N. Y., were visited. At the plant of the Hooker Electrochemical Company the rubber-lined tank car for transportation of C. P. hydrochloric acid was inspected with great interest, as well as the brine purification, electrolytic cells, and caustic evaporation.

Other plants visited were: Niagara Falls Power Co., Niagara Wall Paper Co., Kimberly-Clark Paper Co., and the Shredded Wheat Company.

The meeting ended with both the men and ladies at tea at the beautifully located Niagara Falls Country Club. The meeting proved to be one of the best attended, most profitable from the technical point of view, as well as the most delightful ever held by the Institute.

J. C. Olsen, *Secretary*

Polytechnic Institute
Brooklyn, N. Y.

Society of Chemical Industry Reports

The Council of the Society of Chemical Industry is prepared to offer, on the same terms as last year, *viz.*, at 7s. per copy post free, the Annual Reports on the Progress of Chemistry, Vol. **19**, 1922, to those members of the American Chemical Society whose applications are received by December 31, 1922. Remittances should accompany every order and be made payable, preferably by post-office money order, to Mr. S. E. Carr, Burlington House, London, W. 1, England.

Local Section Officers

At a recent meeting of the Rochester Section of the Society, the following officers were elected: *Chairman:* O. I. Chormann; *Vice Chairman:* E. B. Leary; *Secretary-Treasurer:* E. M. Billings; *Executive Committee:* Charles F. Hutchison, Charles W. Markus, and John F. Murlin.

The Chemical Exposition

The program for the Eighth National Exposition of Chemical Industries, to be held in Grand Central Palace, New York, N. Y., September 11 to 16, 1922, numbers among its speakers not only many of the leading lights in the chemical world to-day, but several of the best-known public men in the United States. Judging from arrangements made so far, the 1922 Exposition program will outstrip those of previous years both in breadth of subjects covered and in the caliber of speakers. Coming between the meetings of the American Chemical Society in Pittsburgh and the American Electrochemical Society in Montreal, the week of the Exposition will probably see the greatest gathering of chemists and chemical business men in the world. With some 450 exhibitors expected, early indications point to a smashing of last year's attendance record of 120,000 visitors.

PROGRAM

Among the prominent speakers are: Wayne B. Wheeler, General Counsel for the Anti-Saloon League and one of the best-known authorities in the United States on alcohol and prohibition legislation, who will speak on the "Attitude of the Anti-Saloon League toward Industrial Alcohol;" and Secretary of Commerce, Herbert Hoover, the "business man of the Cabinet," who will play a part in the Standardization Program in an address to the Salesmen's Association of the American Chemical Industry, entitled "What Standardization Can Do for the Chemical Industry."

During the week of the Exposition the program of each afternoon will be given over to various organizations and subjects. The associations that have definitely arranged to meet include the Technical Association of the Pulp and Paper Industry, the American Ceramic Society, the Technical Photographic and Microscopical Society (September 14, at 2 : 00 P. M.), and the Salesmen's Association of the American Chemical Industry. The Synthetic Organic Chemical Manufacturers Association of the United States is also planning a meeting.

The program of the Technical Association of the Pulp and Paper Industry includes the following papers:

Safety and Efficiency Appliances for the Boiler Plant. W. C. EDGE, Paul B. Huyette Company.

Trimbey and Tibbets Proportioning and Metering System for Paper Stock. J. J. TRIMBEY, Trimbey Machine Works.

Rotary Filters for Washing Paper Pulp and for Filtering and Washing Caustic Lime Mud. (Illustrated.) GEO. D. DICKEY, Industrial Filtration Corporation.

Efficiencies and Economies in Washing Black Liquor from Digested Soda and Sulfate Stock. R. G. WALKER, Oliver Continuous Filter Company.

The Merco Nordstrom Plug Valve. L. D. MILLS, Merrill Company.

Testing Colored Materials for Fastness to Light. H. S. THAYER, Atlas Electric Devices Company.

Instruments for Promoting Efficiency in the Paper Mill. A. E. CAMPBELL, [illegible] Manufacturing Company.

The Carbon Dioxide Record of Combustion Efficiency. C. C. PHELPS, [illegible] Instrument Company.

Steel Belts and Their Application to the Solution of Conveying Problems. [illegible], Sandvik Steel, Inc.

Scott Evaporator as Used in the Paper Mill for Recovering Soda from Spent Liquors. H. [illegible], Ernest Scott & Company.

Dust Protection with Particular Reference to the Use of Respirators. F. M. [illegible], Inc.

The V-Notch Meter and Its Application to the Paper Mill. L. G. CHASE, [illegible].

Continuous Causticizing with Lime Recovery and Re-use. W. D. MOUNT, [illegible] Company.

The Grinnell Dryer Applied to Wall Paper and Coated Paper. JEROME D. [illegible].

The Standardization Program includes the following:

Moderation in Standardization. [illegible], U. S. Geological Survey.

Standardized Testing Apparatus. N. [illegible], U. S. Bureau of Standards.

Discussion of the Reasons for the Varieties of Sizes and Shapes in Glass Bottles. J. C. [illegible] of the [illegible] Container Association.

What Has Been Accomplished in the Standardization of Scientific Apparatus? J. M. ROBERTS, Secretary of the Association of Scientific Apparatus Makers of the United States of America.

Standardization of Fire Clays and Refractories. ROSS C. PURDY, Secretary of the American Ceramic Society, and Chairman of the Committee on Refractories of the American Society for Testing Materials.

Standardization of Enameled Ware for Chemical Purposes. EMERSON P. POSTE, Elyria Enameled Products Company.

Each evening during the week the program has been planned to include motion pictures and illustrated talks, among these are

Prospecting for Gold in Northern Ontario. Courtesy of Ontario Department of Mines.

Assaying for Gold in Northern Ontario. Courtesy of the Ontario Department of Mines.

The Romance of Cotton. Accompanied by discussion and stereopticon slides by DR. DAVID WESSON. Courtesy Southern Cotton Oil Company.

Preparation of Nickel and Securing Copper as a By-product. Accompanied by discussion and explanation. Courtesy International Nickel Company.

The Story of Asbestos. Courtesy U. S. Bureau of Mines and Johns-Manville Company.

Recovering Values from Fume and Smoke.

Inspiration: One of the World's Great Copper Mines.

Mexican Petroleum.

The Story of Heavy Excavating Machinery.

(The above four by Courtesy U. S. Bureau of Mines.)

The Story of Sulfur. Courtesy U. S. Bureau of Mines and Texas Sulphur Company.

The Story of Abrasives. Courtesy U. S. Bureau of Mines and The Carborundum Company.

EXHIBITS

There are already about 400 exhibitors.

Every branch of the chemical and chemical equipment industries, as well as numerous allied houses, will be represented at the Exposition.

The chemical products displayed will include all types manufactured in the United States: Coal, medicinals, and dyestuffs, technical chemicals for the rubber, leather, paper, textile, paint, and other consuming trades,—"everything in chemicals from the crudest of crude materials to the most delicate aromatic ready for the perfumer's use."

A number of new devices in apparatus and machinery developed since the termination of war-time activity and completed since the 1921 Exposition will be displayed for the first time, as well as improvements on machinery long standard for industrial operations. Many of the machines will be seen in actual operation. Some new features which will be on display are:

New special high-capacity evaporator.

Lead pumps for handling phosphoric acid under pressure.

New adaptation of the all hard-rubber pump for use in muriatic acid loading.

Recent development on a balanced automatic control valve and in a direct reading resistance thermometer.

New ideas in pyrometers.

Developments of the past year in butyl alcohol and furfural and their derivatives for solvent purposes.

The use of liquid chlorine in the paper industry in place of bleaching powder.

New dust controlling and humidifying equipment.

New ideas for loading machinery on trucks.

All types of containers, steel fiber, wood, and glass.

The Twenty-ninth Annual Convention of the National Fertilizer Association was held at White Sulphur Springs, W. Va., June 12 to 15, 1922. More than 300 delegates from different parts of the country were in attendance, and the convention was in every respect a success. Business sessions, varied by golf, tennis and quoit tournaments, extended over the four days of the convention and proved to be of unusual interest. Within the last year 62 members withdrew from the Association, but the Secretary's report showed that without any solicitation 9 new members had joined. After hearing the report of the Tariff Committee, the Association adopted a resolution favoring the admission duty free of plant foods.

NOTES AND CORRESPONDENCE

The Industrial Fellowships of the Mellon Institute

The Ninth Annual Report of the Mellon Institute of Industrial Research of the University of Pittsburgh covers the activities and progress of the industrial fellowships during the Institute's fiscal year ended February 28, 1922.

In discussing some of the accomplishments of the system, Mr. Edward R. Weidlein, Director of the Institute, says:

The Industrial Fellowships of the Institute are of two general types, *viz.*, individual and multiple. An Individual Industrial Fellowship utilizes the services of one research chemist or engineer (with assistants when necessary), who is responsible directly to the executive staff of the Institute. A Multiple Industrial Fellowship utilizes the services of one or more research men (Junior Fellows) under the direction of a Senior Fellow, who, in turn, is responsible to the executive staff. There are now (March 1, 1922) thirty-eight Individual and eleven Multiple Fellowships. Since only one investigation is carried out on a particular subject at any one time, and since there is accordingly no duplication of the research activities of the Fellowships, there is always a wide variety of different problems under study.

Three of the Industrial Fellowships now in operation (Nos. 277, 290, and 309) have been effectively at work since 1912, while twenty-one other Fellowships have been promoted continuously

INDUSTRIAL FELLOWSHIPS IN OPERATION AT THE MELLON INSTITUTE ON MARCH 1, 1922

No.	Names of Industrial Fellowships	Industrial Fellows, Names and Degrees	Dates of Expiration
181	Synthetic resins	*C. B. Carter* (Ph.D., University of North Carolina), senior fellow	
		A. E. Coxe (B.S., University of Chicago)	April 1, 1922
233	Enameling	R. D. Cooke (M.S., University of Wisconsin)	April 1, 1922
276	Fish products	D. K. Tressler (Ph.D., Cornell University)	April 1, 1922
277	Bread	*H. A. Kohman* (Ph.D., University of Kansas), senior fellow	
		Roy Irvin (M.S., University of Kansas)	
		E. S. Stateler (B.S., University of Kansas)	June 1, 1922
278	Oil shale	C. L. Jones (M.S., University of Pittsburgh)	June 1, 1922
279	Combustion	J. G. Davidson (Ph.D., Columbia University)	June 1, 1922
280	Protected metals	*J. H. Young* (Ph.D., Ohio State University), senior fellow	
		P. D. Gephart (B.Ch.E., Ohio State University)	June 1, 1922
282	Stove	J. E. Hansen (B.S., University of Illinois)	June 22, 1922
283	Perfumes	J. K. Senior (Ph.D., University of Chicago)	June 15, 1922
285	Food container	W. F. Henderson (M.S., University of Pittsburgh)	
		Adeline Hrubecky (University of Pittsburgh), assistant	July 12, 1922
286	Nickel	R. J. McKay (B.S., University of California)	October 1, 1922
		K. D. Dodds (B.Chem., University of Pittsburgh), assistant	October 1, 1922
287	Metallic oxides	G. E. Seil (M.S., University of Pittsburgh)	September 1, 1922
		C. A. Marsteller (Carnegie Institute of Technology), assistant	September 1, 1922
288	Ester	J. J. Fitzpatrick (B.Chem., University of Pittsburgh)	August 15, 1922
289	Gas	*J. B. Garner* (Ph.D., University of Chicago), senior fellow	
		J. E. Underwood (M.A., Wabash College)	September 15, 1922
290	Oil	*W. F. Faragher* (Ph.D., University of Kansas), senior fellow	
		W. A. Gruse (Ph.D., University of Wisconsin)	
		R. W. Henry (B.S., University of Oklahoma), assistant	
		S. P. Marley (University of Pittsburgh), assistant	
		Ronald Reamer (B.S., Allegheny College), assistant	September 1, 1922
291	Glass	R. R. Shively (Ph.D., University of Pittsburgh)	September 1, 1922
292	Silicate of soda	William Stericker (B.S., University of Wisconsin)	September 8, 1922
293	Slag	Tracy Bartholomew (E.M., Colorado School of Mines)	September 21, 1922
294	Phosphorus	E. E. Marbaker (Ph.D., University of Pennsylvania)	October 15, 1922
295	Salt	T. E. Williams (B.S., University of Michigan)	November, 1, 1922
296	Laundry	*A. F. Shupp* (Ph.D., University of Pittsburgh), senior fellow	
		Alice L. Wakefield (B.S., Carnegie Institute of Technology)	
		Mary M. Danley (B.S., Carnegie Institute of Technology)	November 1, 1922
297	Wood chemicals	R. F. Remler (B.Chem., University of Pittsburgh)	November 1, 1922
298	Emulsion flavors	Melvin De Groote (B.Ch.E., Ohio State University)	November 15, 1922
299	Varieties	E. R. Harding (M.A., Leland Stanford University)	January 1, 1923
300	Inks	F. F. Rupert (Ph.D., Massachusetts Institute of Technology)	November 1, 1922
301	Fiber	M. C. Walsh (Chem. Eng., Columbia University)	November 15, 1922
302	Pratt memorial	(Industrial fellow to be appointed)	December 1, 1922
303	Silicate	J. L. Crawford (B.S., University of Illinois)	December 1, 1922
304	Coke	*F. W. Sperr, Jr.* (B.A., Ohio State University), advisory fellow	
		J. W. Hepplewhite, Jr. (B.Cer.E., Ohio State University)	
		W. J. Huff (Ph.D., Yale University)	
		H. J. Rose (B.A., Yankton College)	
		J. A. Shaw (B.S., Pennsylvania State College)	
		G. G. Desy (B.S., Worcester Polytechnic Institute)	January 1, 1923
305	Organic synthesis	C. J. Herrly (B.S., Pennsylvania State College)	
		H. R. Curme (Ph.D., University of Pittsburgh)	
		F. W. Hightower (B.S., University of Texas)	
		F. H. Marley (B.Chem., University of Pittsburgh), assistant	January 1, 1923
306	Insecticides	O. F. Hedenburg (Ph.D., University of Chicago)	January 1, 1923
307	By-product	Walther Riddle (Ph.D., University of Heidelberg)	
		H. E. Gill (M.S., University of Pittsburgh), assistant	January 1, 1923
308	Fertilizer	*H. H. Meyers* (B.S., University of Pennsylvania), senior fellow	
		Carl Elschner (Ch.E., Institute of Technology of Coethen), assistant	January 5, 1923
309	Glue	R. H. Bogue (Ph.D., University of Pittsburgh)	
		C. K. M. Ritchie (A.B., Oberlin College), assistant	January 5, 1923
310	Asbestos	G. H. Katz (B.S., Ohio State University)	February 1, 1923
311	Metal ware	W. G. Imhoff (M.S., University of Pittsburgh)	February 16, 1923
312	Vitrified tile	H. G. Schurecht (B.S., University of Illinois)	March 1, 1923
313	Insulation	R. H. Heilman (B.S. in E.E., University of Pittsburgh)	January 1, 1923
314	Synthetic acids	R. B. Trusler (B.S., Syracuse University)	February 1. 1923
315	Ozone	E. W. Felkel (B.Chem., University of Pittsburgh)	March 1, 1923
316	Roofing	H. C. Hoover (A.B., Ursinus College)	January 16, 1923
317	Dental alloy	C. C. Vogt (Ph.D., Ohio State University)	February 1, 1923
318	Magnesia products	H. W. Greider (M.S., University of Kansas)	March 1, 1923
319	Dentifrice	*C. C. Vogt* (Ph.D., Ohio State University), advisory fellow	February 1, 1923
320	Refractories	*R. M. Howe* (M.A., University of Pittsburgh), senior fellow	
		S. M. Phelps (University of Toronto)	
		R. F. Ferguson (B.S., University of Pittsburgh)	
		W. R. Kerr (University of Pittsburgh), assistant	March 1. 1923
321	Pharmaceutical	A. W. Harvey (Ph.D., University of Pittsburgh)	March 1. 1923
322	Cleaning	*L. E. Jackson* (B.S., University of Kansas), senior fellow	
		Helen E. Wassell (B.S., Carnegie Institute of Technology)	March 1, 1923
323	Soda	H. G. Elledge (Ph.D., University of Pittsburgh)	March 1, 1923
325	Vitrified tile	H. G. Schurecht (B.S., University of Illinois)	March 1, 1923

for three or more years, and eleven Fellowships are in their second year of operation.

These Fellowships are all well established in their fields of inquiry; and their renewal, year after year, attests to their productivity and to the confidence which their donors have in the Institute. It is of interest to mention here that the incumbents of the larger and older Industrial Fellowships are recognized generally as specialists in the specific branches of technology in which they are carrying out investigations.

The following eleven Fellowships have been founded by associations:

No.	NAME	Company-Members in Association
282	Stove	14
296	Laundry	1901
297	Wood chemicals	68
301	Fiber	25
306	Insecticides	7
311	Metal ware	14
312	Vitrified tile	19
318	Magnesia products	2
320	Refractories	98
322	Cleaning	9
325	Vitrified tile	25

Industrial Fellowships established by associations of manufacturers[1] not only enable the Institute to be of direct service to groups of industrial concerns instead of to individual companies, but their successful operation also gives rise to more stable relations of coöperation among the company-members of these associations by the induction of the reciprocal exchange of experience and research results. The Institute acts as a clearing house of information for donating associations, and gives all the assistance and advice in its power to the company-members. In illustration of this function of the Institute, it may be mentioned that Multiple Industrial Fellowships are supported by the Laundryowners' National Association, the Refractories Manufacturers' Association, and the International Technical Society of Cleaners and Dyers. These Fellowships, which are representative of the others of this general class, serve as technical advisers to the individual members of the donating associations, in addition to conducting testing, standardization, and research work of general importance. For the most part, the research has to do with the improvement of industrial processes.

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[1] The system in operation at the Institute contemplates that the association shall be limited in each case to those firms in an industry whose interests are sufficiently homogeneous to induce them to pool their resources for the purpose of research.

Universities, Buy American Chemicals!

Editor of the Journal of Industrial and Engineering Chemistry:

The chemical departments of the various colleges and universities have been producing great numbers of chemists. These men in large measure are looking for jobs, and an army of graduates is just now swelling the number.

It happens that the chemical industry is not in the best position just now to absorb our graduating chemists, but nevertheless the obligation is strong upon us, for the sake of the future of the American chemical industry as well as the present, to take [illegible]

But is there not also an obligation on the colleges? In our rare chemical business our distributors encounter two classes of buyers or purchasing agents in the universities.

The first class buy as a matter of broad-minded policy; the second as a matter of sharp business. The first endeavor to support American industry because they and their graduates and undergraduates are, or will be, a part of it. The second class buy because their idea of their duty is that they must buy at the lowest possible prices, regardless of anything else. They are not concerned with the fact that unless a fair adjustment of the tariff is made, large sections of the American chemical industry will disappear, and consequently jobs for their graduates and money for their colleges from a healthy industry. A healthy industry means gifts to the support of the chemical department, many of whose buyers are now penny wise and pound foolish.

When an ounce of gold buys at least twelve times as much expert labor in countries with depreciated currency as in America, the American manufacturer, although he reduces his prices below the starvation point, cannot meet foreign prices generally.

The purchasing agents in many cases are buying foreign products, even when the differential is a very small one. Their position is that they were appointed to buy at the lowest prices and that no one has given them authority to set patriotism or the ideal of promoting the chemical industry in America above the considerations of business. They may be right, and if so what I have to suggest should be taken up with the professors who specify and with those university authorities responsible for ideals and policy.

My suggestion is that each chemist looking for a job (and jobs are not so plentiful now in chemistry as they might be) go or write to the purchasing agent of his alma mater and ask this question, "How do you expect American chemists to find jobs unless all buyers of chemicals, and especially and above all the institutions which made us chemists, buy American chemicals?"

The editor of THIS JOURNAL, I believe, will be very much interested in the replies made to this question and they should be reported to him.

CARL PFANSTIEHL

SPECIAL CHEMICALS CO.
HIGHLAND PARK, ILL.

June 13, 1922

Japan Letter

By K. Kashima

1125 IKEBUKURO, NEAR TOKYO, JAPAN

It is a great pleasure to be invited to write a monthly letter on the progress of chemical science and industry in Japan. Friendship is developed from mutual understanding. American periodicals, books, machines, chemicals, and many other goods are continually being imported to this island, and they indicate America's progress to the Japanese. Our goods go to America also, but almost none of our periodicals or books. The Japanese generally use Chinese characters with Japanese "kana," which are difficult for foreigners to understand. It is therefore a pleasant duty to communicate the present status of chemical science and industry to the members of the AMERICAN CHEMICAL SOCIETY.

To explain the present state of chemical science and industry in Japan, it would be necessary first to write their history. The development of modern science and industry in Japan begins with the Meiji Era (1868–1912). Before this time there existed, of course, some chemical science and industry, but it could hardly be called such, since it was confined for the most part to mere personal experiences. After the Imperial Government displaced the Tokugawa-Shogunate, western civilization flowed into these islands and the Japanese endeavored to master chemical science.

The progress in the Meiji Era was enormous, but it was gradual. After the outbreak of the Great War, industry, especially chemical industry, made rapid and sudden progress. Almost all chemical products were manufactured by us and exported to other countries. Capital devoted to industry was increased and factories were rapidly built, especially in the neighborhood of Tokyo, Osaka, and the northern part of Kyûshû. Then the war came to an end and panic visited every factory. Conditions are still no better. A few days ago the Association of Chemical Industry held a meeting to discuss the situation, and it was decided to appeal to the government for higher import taxes on some of the important chemical products.

June 21, 1922

LONDON LETTER

By Hugh Griffiths, 15 New Bridge St., London, E. C. 1, England

The Safeguarding of Industries Act

The Key Industries bill is still engaging close attention, and two very interesting complaints have been heard by the Official Referee. Hitherto, in most of the complaints, discussion has been directed towards ascertaining the meaning of the term "fine chemical;" in the case of "synthetic camphor" the discussion was more particularly directed to fixing the meaning of the term "synthetic." The decision of the Referee, which was given at great length, cannot be considered as other than masterly, and one feels, after reading this decision, that the synthetic chemical has been put in its place once and for all, and that the limitations of the term "synthetic" have been defined for the benefit of posterity. The essential point of the award is that both pinene and synthetic camphor are removed from the list, and Komppa's synthetic camphor added.

Some very interesting facts were disclosed in the course of evidence, a witness stating that one firm purchased camphor during 1913 to the value of £100,000. The difficulties imposed upon the producers of turpentine camphor by the Japanese producers of natural camphor were also mentioned. Most chemists will feel that it is unfortunate that an important industry such as the production of turpentine camphor should be completely beaten out of existence, and it is common knowledge that every concern which has attempted to produce this material commercially in England has been subsequently compelled to abandon its operations. The experience in the United States has been somewhat similar.

A complaint regarding incandescent gas mantles has also been heard, and it has been decided that incandescent gas mantles, being "mechanical aggregates of oxides of thorium and cerium," are included in the phrase "compounds of thorium and cerium, etc.," and are to be included in the list. A further inquiry is now being held under Section 2 of the Act, and an endeavor is being made to get a duty of $33^1/_3$ per cent imposed on all incandescent mantles imported from Germany.

British Dyestuffs Industry

During the war it was reported in this country that a very subtle individual had succeeded in obtaining all the "secrets" of dye manufacture, as practiced in Germany, and that the documents were on the way from Switzerland, securely packed in a foreign office bag. This statement was met with great scorn by technical men, and it was pointed out that the accumulated experience of forty years could not be so easily lifted.

A disquieting announcement has now been made, that the representatives of the British dye manufacturing concerns are in negotiation with the German producers at the present moment, with a view to securing coöperation in some form. It is of course well known that the producers of dyestuffs in this country have been losing money for some time, and it is not surprising that these negotiations are in progress. The question arises, however, whether any good can come from these conversations, which must be regarded in the nature of a confession of failure. This matter is very strongly discussed in technical circles, where it is fully realized that mere recipes and information regarding the technic of manufacturing processes will not be sufficient to save the industry.

The essential difficulties of the British dye industry may appear at first to be technical difficulties, but it must be remembered that all the plants were put down at a time when market conditions were quite artificial, and since the various works were designed the market conditions for every product have received rude shocks.

Even under conditions of normal demand and steady markets the organization of a dye industry, with its interlocking ramifications, is no mean problem. At a time when the world's markets are in a state of upheaval, proper organization and coördination of the various activities are almost beyond human powers, and steady efficient working of manufacturing plants cannot possibly be achieved, nor could all the accumulated skill and technical experience in the whole of Germany, or elsewhere, solve this problem at the present time.

It is felt in this country that, at any cost, this industry must not be allowed to collapse, and that the only solution lies in adequate financial support until the industry can work out its own salvation.

Fine Grinding and Incorporation

Since the somewhat bitter controversy between Gates and Stadler, very few contributions to the theory of fine grinding have been made, and the study of the energy efficiency and the mechanism of pulverization has been handicapped to some extent by the difficulty of obtaining a satisfactory means of grading powdered materials of a fineness much below 200 mesh. In this connection, the investigations made by Dr. T. M. Lowry in England are of special interest.

At a recent joint meeting of the Faraday Society and the Oil and Colour Chemists Association, this subject was discussed. While many of the advantages of grading by means of air currents were pointed out and fully appreciated from the commercial point of view, a precision apparatus for elutriation tests was described, and the various conditions controlling the accuracy of the instrument detailed. Apparently this instrument was designed to provide a satisfactory test for barytes for works use, and probably will be applied to the study of the products from fine grinding machines. A particularly interesting field of application should be in the study of the coarser products of the colloid mill.

Another important subject has been investigated by E. P. Perman, namely, the testing of the degree of incorporation of explosives and similar materials. While it is a simple matter by ordinary analytical methods to study the coarse mixing of materials in a mill, it has been pointed out by Perman that in order to secure a test of incorporation very minute samples must be taken, and in the case of the mixture chosen, containing ammonium nitrate and TNT, samples of about 1 mm. each were examined by a Nessler method. The figures of mean deviation enabled the effect-variations in time of milling, weight of charge, and miling speed, to be traced accurately.

The Colloid Mill

Great interest has been shown in this country in Plauson's colloid mill. This machine has been specially designed for the reduction of materials to very small dimensions, in some cases down to 0.01 μ.

The writer has had the privilege of seeing one of these machines in operation at Erfurt, and has also been able to discuss the mill with the inventor, and Herr Block of Emil Passburg Maschinenfabrik, who was responsible for the mechanical details of the design.

The machine consists of a circular casing, with an eccentrically placed rotor which is driven at a very high peripheral speed. The casing contains a liquid, and the machine therefore consists, in principle, of an impact disintegrator in which the material is pulverized in the presence of a liquid. With this device, it is claimed, a much larger proportion of small particles of the order of magnitude of 0.01 μ can be obtained, than in any dry disintegrator or in any ordinary system of wet grinding. The claims appear to be established, and the commercial possibilities of the machine look interesting.

It is possible, by the use of dispersion accelerating agents, to increase the production of fine particles and to produce stable emulsions and dispersions in the machine, from all kinds of materials. Mercury can be dispersed in water to the form of a stable colloidal mercury of high concentration. The machine has also been applied to the production of colloidal fuel, homogenized milk, viscose, lubricants, and many other materials. Most of these substances have been treated experimentally with very interesting results, but so far as this country is concerned little is known regarding the commercial exploitation of the machine.

Several German firms have installed machines for commercial use, but it is fairly obvious from the scope which this machine offers, that it will be some time before the commercial applications can be fully investigated. It is at present extremely difficult to say which of the applications will prove profitable, but from a scientific point of view the results will be looked for with very great interest.

Plauson's Ultra-Filter

The inventor of the colloid mill has also patented some new types of filtering surface of adjustable porosity. The apparatus shown to the writer at Erfurt consisted essentially of a cylindrical chamber made of rings of metal with slotted perforations. The pressure on this bundle of rings could be adjusted by means of screws, and when cleaning was required the pressure could be removed. This arrangement gave a filtering surface which could be adjusted and easily cleaned, the mixture to be filtered being pumped into the interior of the built-up cylinder. The solid material deposited was removed by a spiral, the machine operating continuously in a manner somewhat similar to the well-known extraction press.

The writer saw this apparatus working on a mixture of china clay and water, and it appears that modified constructions have been produced capable of filtering out the dispersed materials obtained, by means of the colloid mill.

According to the technical data given by Dr. Plauson, even with colloidal materials large performances per unit filtering surface can be obtained, and there appears to be a wide range of possibilities of commercial application for this machine, as soon as the production has been organized.

June 22, 1922

PARIS LETTER

By Charles Lormand, 4 Avenue de l'Observatoire, Paris, France

As I said in my previous letter, I shall report on the International Conference of Pure and Applied Chemistry held at Lyons, and the National Congress of Industrial Chemistry at Marseilles.

CONFERENCE AT LYONS

The Conference at Lyons commenced June 27, with 22 delegates, representing 22 countries, present. That the number of nations represented increases from year to year confirms the success of these conferences. I know very well that a larger number of nations would like to be included, but it is still too early to open the gates too wide, as it is essential that a minimum of cordiality be maintained, and the situation of international politics, unfortunately, prevents this minimum of cordiality.

A number of reports were presented by the Commissions, of which each nation had a member. After discussion and some modifications, these reports were presented to the Bureau of the Union, which ratified the conclusions, with some modifications.

The **Commission on Nomenclature of Mineral Chemicals** has decided that in all tables the names of metals or positive groups be put in the first column, and in the second line the names of the negative elements following, for example: (1) Copper, (2) Sulfate. This Commission, thinking that the Formula Index, used in *Chemical Abstracts*, gives complete satisfaction for the classification of mineral compounds, will urge publications to adopt this classification as soon as practicable.

The **Commission on Organic Chemistry** decided that all questions concerning nomenclature be sent to them for consideration, and should be reported to the editors of the most important journals of chemistry.

In 1923 the Commission will issue a report in view of forming a complete system of nomenclature, to be adopted by the leading scientific journals. This report will be prepared by Mr. Greenway and Marquis Petterson, and will be sent to the six chairmen of the committees of the nations: Messrs. Angeli, Billman, Blaise, Norris, Smith, and Votocek.

The **Commission on Signs of Potentials of Electrodes** has made the following decisions: (1) Whenever mention is made of the potential of a metal in a solution, the sign of the potential of the metal should be used; (2) when a numerical value of a potential is given, the basis of the reference should be indicated, with all the details necessary for its reproduction.

The **Commission on Chemical Periodicals** reports the following: (1) The abbreviations used by *Chemical Abstracts* are not desired. The abbreviation for the word "Japanese" is to be "Japan" and not "Jap." (2) Various opinions concerning the use of the decimal system by the International Institute of Bibliography and also the function of the Office of Documentation were put on record. (3) All publications shall bear the address of the author, or of the laboratory where the work was done. (4) All articles shall include a synopsis of the article by the author, which will be used for abstracts, following the example of the *Journal of Industrial and Engineering Chemistry*.

Chemical Standards—The operation of the different national institutes was regulated. Particular interest was shown in the use of analyzed samples coming from the United States through the Bureau of Bruxelle. The Bureau of Paris for technical samples is similar in function.

For thermochemical standards, benzoic acid has been adopted, as prepared by the Bureau of Standards of Washington and through the Bureau of Bruxelle. The value of 6.324 calories [illegible] has been adopted.

The agreement between the American Committee on Critical Tables and the International Committee on Annual Tables is recorded.

Each country shall bring to the next Conference suggestions as to proper legislation concerning authorized antiseptic products, so that the following year a list of antiseptics may be published in each country. The work of the Bureau of Agriculture was mentioned, and, as, in spite of their conclusions, the use of certain antiseptics is permitted in the United States, it is requested that each nation consider anew the possibility of studying antiseptics.

The nomenclature of solid and gaseous combustibles, together with the analytical methods used for their control, will be fixed in each country, and the results obtained will be subjected to the consideration of the next International Congress.

The **Commission on Patents** named a delegate to confer with each government for the purpose of establishing international patents.

The **Commission on Industrial Hygiene** asked each country to bring to the next Conference the results of an investigation on legislation and precautions used for the suppression of factory dusts and fumes.

The members of the Conference visited all the factories of the Lyons region. They also heard three interesting papers: one by Mr. Vignon, Professor at the Faculty of Science at Lyons, on "The Origin of Artificial Organic Coloring Matter;" and one by Mr. Perrin, on "The Actual State of the Atomic Theory," and one on "Radio-Chemistry."

The Bureau of the International Union was reäppointed, as follows: Sir William Pope, President, Messrs. Paterno (Italian), Bancroft (American), Billman (Danish), and Votocek (Czecho-slovakian).

The next Conference will be held in June 1923 at Cambridge, England, following the suggestion of Dr. Charles L. Parsons. The Conference of 1926 will be held at Philadelphia, Pa.

The Conference ended by the departure of all the delegates of the Union for Marseilles, going down the Rhone by boat.

CONGRESS OF MARSEILLES

At Marseilles the members of the Conference met again the members of the National Congress of Chemical Industry, and began their sessions with Mr. Girard presiding. I had the honor of presenting at this first reunion the film on the sulfur industry of the United States, obtained from the Bureau of Mines at Washington. This film especially interested the Italian delegates as well as those who refine sulfur in Marseilles.

The Congress listened to an important address by Mr. Matignon on "The Actual State of the Nitrogen Industry," and one by Mr. Sabatier, winner of the Nobel Prize in Chemistry, on "Hydrogenation of Oils."

The Congress ended with visits to all the factories of the region and an excursion to the salt works of Giraud, where Ball ard discovered bromine.

We had the pleasure of having at the Conference and the Congress a number of American delegates, and we were proud to show them our factories and were honored by the appreciation which they accorded to our industries.

July 1, 1922

Letters received from Dr. Atherton Seidell, who attended these conferences at Lyons and Marseilles, are very enthusiastic in commendation of the excellent organization, even to minute details, of the meetings, and also in appreciation of the splendid hospitality shown the delegates.

WASHINGTON NOTES

Muscle Shoals

The Muscle Shoals controversy is to be fought out on the floor of the Senate. There are indications that the fight will be a bitter one. The Senate Committee on Agriculture, after months of hearings and a personal inspection of the whole Muscle Shoals project, has failed to agree on a majority report favoring any of the plans submitted. The Henry Ford proposal, which received the greatest number of votes, was rejected by a vote of 9 to 7. The bill introduced by Chairman Norris, providing for operation of the project by the Government, was likewise rejected by a vote of 9 to 5. The other offers, including those of the Alabama Power Co., Frederick E. Engstrum, and Dr. Charles L. Parsons, were rejected, but without a record vote. The committee then agreed to submit two minority reports to the Senate. Senator Ladd will accordingly present a minority report urging the acceptance of the Ford proposal. The bill that he will advocate is the same as the Wright bill, which was favorably reported by the House Committee on Military Affairs after months of exhaustive investigations, and is the original Ford offer as modified by the House Committee and approved by Mr. Ford. The second minority report of the committee will be presented by Senator Norris and will provide for a government-owned and controlled corporation of the entire Shoals project. Both reports, members of the committee announce, will be submitted at an early date.

When the House reconvenes the middle of August it will very probably give prompt attention to the Muscle Shoals situation. It will be recalled that the House was very reluctant to agree to the Senate amendment appropriating $7,500,000 for construction work on the Wilson Dam. In the belief that final decision would be reached on the Muscle Shoals project prior to October 1, the House finally agreed to the Senate amendment, but with the proviso that the money, instead of becoming immediately available, should not be available until October 1. The Senate, after very bitter opposition, finally concurred in the House amendment. Both houses of Congress thus offer very fertile field for debate on this much-mooted question.

The situation in brief is just this. The committees in both branches of Congress charged to study and investigate this problem have completed their work, and have submitted, or will very shortly submit, their findings to their respective bodies. In other words, the next move is to fight the whole Shoals question out on the floor of the House of Representatives and the Senate of the United States. Just when this fight will be begun and completed is a matter for conjecture.

Joint Committee Recommends Standards for Food Products

The Joint Committee on Definitions and Standards, at a recent meeting in Washington, D. C., recommended the adoption of standards or modifications in existing standards for condensed milk, evaporated milk, concentrated milk, butter, renovated butter, cacao products, ginger ale flavor, and ginger ale.

Heretofore the decisions of the joint committee have not been published until they were presented either at the annual meeting of the Association of Official Agricultural Chemists or of the Association of American Dairy, Food and Drug Officials. The joint committee at its recent meeting authorized the chairman to make public at once all affirmative recommendations; because, in its opinion, the delay in waiting to announce decisions until the meetings of the associations often worked a hardship on the industries affected.

Dye Embargo

On July 15 the Senate, by a vote of 38 to 32, rejected that portion of the Tariff bill which provided for the continuation of the existing emergency dye embargo for one year after the passage of the bill. The roll call on the amendment was as follows:

For the Embargo

Republicans

Ball
Brandegee
Bursum
Calder
Curtis
du Pont
Edge
Ernst
Fernald
France
Frelinghuysen
Gooding
Hale
Jones (Washington)
Ladd
Lenroot
Lodge
McCumber
McKinley
McLean
McNary
New
Oddie
Pepper
Phipps
Rawson
Shortridge
Sterling
Townsend
Warren
Watson (Indiana)
Willis

Against the Embargo

Republicans

Borah
Capper
Cummins
Harreld
Johnson
Kellogg
Keyes
McCormick
Moses
Nelson
Nicholson
Norbeck
Norris
Smoot

Democrats

Ashurst
Caraway
Culberson
Dial
Fletcher
Harris
Harrison
Heflin
Kendrick
King
Oberman
Pomerene
Ransdell
Robinson
Sheppard
Shields
Simmons
Smith
Stanley
Swanson
Trammell
Underwood
Walsh (Massachusetts)
Walsh (Montana)

Not Voting

Broussard
Cameron
Colt
Crow
Dillingham
Elkins
Gerry
Glass
Hitchcock
Jones (New Mexico)
La Follette
McKellar
Myers
Newberry
Owen
Page
Pittman
Poindexter
Reed
Spencer
Stanfield
Sutherland
Wadsworth
Watson (Georgia)
Weller
Williams

But this does not mean that the dye embargo is lost. Two amendments have been drafted and will be presented to force another vote in favor of the embargo when the Committee of the Whole reports the bill back to the Senate. Senator Frelinghuysen has announced that at that time he will again present the embargo provision, and Senator Bursum is preparing an amendment to continue the embargo for a year or more, but with the added provision that the profits of the dye manufacturers in excess of 10 per cent be paid into the United States Treasury.

The Senate amendment to the Army bill increasing the appropriation for the Chemical Warfare Service from $500,000 to $750,000 was not approved by the conferees and the bill as finally passed carries an appropriation of only $600,000 for the Chemical Warfare Service for the fiscal year which began July 1. This appropriation will be devoted mainly to research and development and for training in defensive chemical warfare.

Mr. E. O. Reed, who for a number of years has been assistant chemist in the Leather and Paper Laboratory of the Bureau of Chemistry, was transferred on July 1 to the Government Printing Office as chief of the new Testing Section. Mr. Reed has been detailed to the Government Printing Office since February 1922 to assist in organizing the testing work. The purpose of the laboratory is to test the supplies furnished to the Government Printing Office on contract and conduct plant research work.

The Division of Dehydration of the Bureau of Chemistry has been transferred to Los Angeles, and combined with the other work of the Bureau at that point, with Mr. E. M. Chace in charge. All the people who were connected with this investigation in Washington have been transferred to Los Angeles. The change was made because so many of the products utilized in dehydration are grown on the Pacific Coast, and also because it was believed to be advisable from an economical standpoint to combine the work, since Mr. Chace has organized a laboratory for studying the utilization of fruits and vegetables.

The coöperative arrangement between the Central of Georgia Railway Company and the Bureau of Mines, whereby $6000 is made available for continuing the investigation of Georgia clays and bauxites has been continued. This is the second year of the coöperative agreement. The first year's work proved to be very interesting and records a new method of purification of the clays for use in white ware and also the possibility of the use of certain Georgia clays for refractories.

Dr. J. A. Ambler has been appointed chemist in charge of the Color Laboratory of the Bureau of Chemistry. With the exception of a few months, Dr. Ambler has been acting chief since Dr. H. D. Gibbs resigned about three years ago.

Dr. F. P. Veitch of the Bureau of Chemistry has been appointed by the Secretary of Agriculture as a member of the special committee on government paper specifications. This committee will prepare and submit to the Congressional Joint Committee on Printing specifications for paper for public printing and binding.

Personals

The Franklin Institute has awarded to **Prof. Eugene C. Bingham** of Lafayette College its Certificate of Merit for his Improved Variable Pressure Viscometer.

Dr. Robert Calvert, formerly a laboratory director for E. I. duPont de Nemours & Co., and later of the University of Southern California, is now employed by the Celite Products Co., as research engineer in charge of their laboratory at Lompoc, Cal.

Dr. Paul M. Giesy, formerly with the Calco Chemical Co., Bound Brook, N. J., is now research chemist with E. R. Squibb & Sons, at their Brooklyn plant.

Mr. Arthur Grounds, formerly chief chemist to the Sun Co., Ltd., Swansea, is now associated as consulting chemist with Mr. Harold Moore in Manchester, England.

Mr. Henry W. Hess, consulting chemist of Toledo, specializing in the glass industry and in the adaptation of special fuels to special purposes, has gone to England on an important problem relative to the production of the Osram lamp.

At a recent meeting of the Board of Directors of the Air Reduction Co. ,Inc., **Dr. Floyd J. Metzger** was elected vice president in charge of research and development.

Mr. E. A. Wilson, director of the Pyralin Research Laboratory of E. I. duPont de Nemours & Co., is resigning to engage in the practice of chemical engineering.

Dr. J. W. Turrentine, formerly director of the Experimental Kelp-Potash Plant of the U. S. Department of Agriculture at Summerland, Calif., has obtained furlough from the Department for a period of six months to act as consulting chemist for the U. S. Kelp Products Corporation, the newly organized concern which has purchased the government's plant and is now proceeding with the manufacture of kelp products.

Mr. C. E. Betz has been appointed chief chemist of the Pittsburgh Testing Laboratory. **Mr. Mercer B. Mayfield, Jr.**, is to succeed Mr. Betz as chemist-in-charge of the New York Laboratory of the company.

Dr. Elbert C. Lathrop has severed his connection with E. I. duPont de Nemours & Co., Inc., Wilmington, Del., to become vice president and treasurer of Samuel P. Sadtler & Son, Inc., Philadelphia, Pa. Dr. Lathrop will devote his entire time to consulting work and to the study of industrial engineering problems.

Mr. R. E. Zimmerman, formerly director of the research laboratory of the American Sheet & Tin Plate Co., has been made assistant to the vice president. **Mr. J. W. Whetzel**, formerly research associate, has been appointed manager of the research laboratory, and **Mr. E. S. Taylerson**, formerly physicist, is now assistant director.

Mr. Theodore F. Bradley has left the Sherwin-Williams Company to become chemist for the Mica Insulator Co., Schenectady, N. Y.

Mr. T. G. Greaves has resigned his position as chemist of the American Dyewood Company's Mobile, Ala., plant to become chemist of the International Cotton Protecting Co., Mobile.

Mr. R. L. Howard, associate professor of chemistry in the Medical College of Virginia, has been awarded the Research Fellowship in Pharmacology at Western Reserve University.

Dr. G. F. Reddish has been elected associate professor of bacteriology at the Medical College of Virginia.

Dr. Paul A. Warren has been elected professor of botany, School of Pharmacy, Medical College of Virginia.

Mr. G. G. Crewson has resigned the plant managership of the Refractory Products Corporation plant at Index, Va., to become associated with the engineering staff of the National Aniline & Chemical Co., Buffalo, N. Y.

Mr. Austin Bailey has resigned his position as assistant professor of physics in Kansas University to accept a position in the Radio Department of the American Telephone & Telegraph Co., New York City.

Mr. C. W. Crowell has resigned as chemist of the California & Hawaiian Sugar Company to accept a position as superintendent of the Rochester Germicide Co., Rochester, N. Y.

Prof. Charles S. Bisson has left the South Dakota School of Mines to take charge of the Department of Chemistry at the Northern Branch of the University of California, Davis, Calif.

Industrials

A research fellowship of $1000 for the study of the chemistry of the *tubercle bacillus* has been given to Yale University by the National Tuberculosis Association. The funds will be used to support research in the subject now being conducted by Prof. Treat B. Johnson and Dr. E. B. Brown.

E. I. duPont de Nemours & Company announce that they have developed and placed on the market a new dye to be known as Pontachrome Brown SW, which may be used on woolen goods, either as a self shade for producing full rich browns or as base for the production of a pleasing range of dark brown shades, and which is especially suitable for suitings containing unresisted silk effects.

At a meeting of the directors of the Heyden Chemical Company of America, held June 27, the following officers were elected: President, Bernard R. Armour; vice president, James Branegan; chairman of the board, Frederick Chamberlain; directors, Bernard R. Armour, George L. Armour, James Branegan, William Weckman, S. S. Theil, and Mr. Smith.

While in 1912 about 2,500,000 lbs. of artificial silk were used in this country, nearly 20,000,000 lbs. were used in 1921. The domestic production of this material increased from almost nothing in 1910 to nearly 20,000,000 lbs. in 1921, or about 50 per cent as much as the total consumption of natural silk for the same year. Before 1915 over 75 per cent of the artificial silk was used in the manufacture of hosiery, while now only about 40 per cent is so used.

The Combustion Engineering Corporation has issued in pamphlet form a paper on "Powdered Coal Application to Four 2640-H. P. Boilers," which was presented before the Engineers' Society of Western Pennsylvania in 1921 by H. D. Savage.

The Electric Furnace Construction Co., of Philadelphia, Pa., has announced the appointment of the following officers: President, Frank Hodson; vice president and treasurer, P. H. Falter; vice president and counsel, Arthur G. Dickson; new directors, John Gilbert, Wm. A. Webb, and T. H. Weisenburg.

The Swenson Evaporator Company has become a subsidiary of the Whiting Corporation of Harvey, Ill.

The Nordmont Chemical Co., Nordmont, Pa., manufacturer of charcoal, wood alcohol, and by-products, has been sold, and is to be dismantled as soon as the supply of chemical wood on hand has been exhausted.

The National Aniline & Chemical Co., Inc., has just issued its customary booklet of Dyer's Formulas for the fall season shade card, issued by the Textile Color Card Association. Formulas are given for dyeing on skein silk under each one of the same established by the Association, and following this a similar treatment is given the formulas for dyeing cotton, this being divided into three methods: for light shades secured by direct dyes on cotton, for medium and dark shades secured by direct dyes on cotton, and for basic dyes on cotton with tannic acid. Acid colors on wool and chrome dyes on wool are next treated, as well as leather dyeing in two methods, *viz.*, one for dyeing 100 lbs. of chrome tanned leather, and the other for dyeing 100 sq. ft. of vegetable tanned leather.

The Brown Instrument Co., Philadelphia, Pa., has published a new resistance thermometer catalog, which explains the theory of resistance thermometry, the various types of instruments which are made, the merits of each type, and the field covered by these instruments. It is claimed that for installation where extreme accuracy is required within a very small range of temperature, the electrical resistance thermometer is the best instrument yet produced.

The Schutte & Koerting Co., Philadelphia, Pa., has issued a new catalog describing mechanical fuel oil burning systems and fuel oil burners in which the oil is atomized by low or high pressure air and steam. It discusses the installations, operation and maintenance of oil burning equipment, its characteristics, requirements and functions, the relative merits of mechanical and spray oil burners, the design, purpose and operation of air control registers, oil pumping outfits, duplex oil strainers and fuel oil heaters, the general requirements of steam boiler furnaces for burning oil, operation and inspection of the system, lighting the fires, air for combustion, indication of satisfactory operation, number and arrangement of burners, effects of carbon deposits and soot, etc.

BOOK REVIEWS

Catalytic Action. By K. George Falk. The Chemical Catalog Co., Inc., New York. 171 pp. Price, $2.50 net.

This is a continuously readable and interesting review of the subject. While the author has covered the whole field from the history, in "General Views," to visions, in" Life Processes," he has kept constantly in mind a useful conception of one way in which catalytic reactions may occur. Whether they all actually occur in that way is much less important than the fact that the reader is given an interesting and up-to-date picture of the subject.

To his mind, all catalyses may involve a combination or "addition" of all the different substances present and a subsequent decomposition into the final products, his criterion of catalysis being that the "composition of one of the initial substances is the same as that of one of the end-products." In this way he includes what has been called negative catalysis and visualizes catalytic reactions in which there is no actual change in velocity. He has not hesitated to describe, in a chapter on "Recent Theories," most of the various attempts to use absorption of radiant energy in chemical reactions, and he discusses the modern papers of Einstein, McLewis, Tolman, Langmuir, Dushman, Baly, etc. He shows how the work of Stieglitz on imido esters contributes to recent advance. The presence of acid accelerates the hydrolysis or decomposition, because these esters are very weak bases which form highly ionized salts. The ion concentration determines the velocity, and this catalysis thus comes under concentration-effects. It is natural to want to apply such information to the catalysis by enzymes and to the many complicated cases in which the hydrogen or hydroxyl-ion concentration so enormously affects the different enzymes. The author here points out the present incomplete state of this part of the subject; yet he arouses in the reader an interest in recent research work, such as that of Loeb, on proteins and colloid behavior.

In the chapter on "Contact Catalysis," the thought is induced in the reader's mind that through further application of the studies of physical or chemical reactions at surfaces, a new story of general catalysis may be sought. Adsorption has become chemical reaction in a plane, and here other reactions may occur. They are all based on electronic or magnetic field effects, so the application of the resulting laws and statistical atomic mechanics to three dimensions, or mass-action, seems foreshadowed.

The gradual application of the results of study of surface catalysis in processes where the colloidal state of a reagent is evident, and then to such less obviously heterogeneous reactions as enzyme catalysis, is now to be expected, and the applications to cases of simple solutions should follow.

Each of the eight chapters is an interesting, instructive entity.

The author refers liberally to the recent literature, and he summarizes for the general chemist the present state of knowledge, even where he is obliged to point out its incompleteness.

My own feeling, on finishing this book, was that the author had seen in Langmuir's work the opening wedge to much new physical chemistry which is fundamental to catalysis. I should like to read the book, which he or another will doubtless later write on the subject, beginning where he now leaves off, "Contact Catalysis." This book will probably begin with the simple chemical reactions in molecular layers, with due deference to the physical or electrical structures which we have for years attributed to different molecules without apparently believing that they practically or pragmatically exist

W. R. Whitney

Sewerage and Sewage Treatment. By Harold E. Babbitt, Assistant Professor Municipal and Sanitary Engineering, University of Illinois. 512 pp., 186 figs., 103 tables. John Wiley & Sons, Inc., New York, 1922. Price, $5.00 net.

The author states that this book is a development of classroom and lecture notes, prepared for use in his classes at the University of Illinois. It covers both sewerage and sewage treatment, much the same ground as does the abridgment of Metcalf and Eddy's treatise, recently published.

In its plan, the book is well adapted to teaching and will serve as a reference book for practicing engineers. Among the subjects which the reader will be pleased to find treated are pumps and pumping stations, contracts and specifications, to which 21 pages are devoted, and the newer processes of sewage disposal, even including a section on electrolytic treatment, the focus of so many trials and the producer of so few results in practice.

The arrangement of the book is excellent, and the examples from practice are well suited to instruction. Particularly instructive are the chapters on sewer design and construction and those on sedimentation and trickling filters. It is unfortunate that in a book intended for students there should be so many arithmetical errors. Examples of this are on pp. 56, 130, and 202, but there are others which need correction.

Ten pages of the book, or one-sixteenth of the space devoted to sewage treatment, are devoted to sludge disposal. The failure to devote more space to this, the most important part of sewage treatment, is not peculiar to the author, but is in line with the development of sewage disposal methods, which, as is well known, pay chief attention to the liquid portion of the sewage.

The book would gain in value if more attention were paid to the treatment of industrial wastes, a matter of growing importance, particularly in the region between the Penobscot and the Potomac, and in portions of the Middle West.

The book can be recommended to any student of the sanitary arts, even those who have graduated into engineering practice.

R. S. Weston

Dyes Classified by Intermediates. By R. Norris Shreve, with the collaboration of W. N. Watson and A. R. Willis. 631 pp. The Chemical Catalog Co., Inc., New York, 1922. Price, $10.00.

The justification for any scientific book is the need it fills in research, manufacture, and commerce. From this standpoint, Mr. Shreve has succeeded in placing before the public a book which is unique because it fills a need which no other book known to the writer has attempted to fill. There is probably no large dyestuffs manufacturer in America who has not been forced to face the problem of orientation in installing and operating intermediate plants. The proper correlation of intermediate and dyestuffs manufacture with the ultimate needs of the consuming industries lies at the root of the successful development of the American dyestuffs industry. Any compilation of facts which aids in the establishment of such correlation is of first aid to the industry, and, irrespective of its scope, will be welcomed because it fills a real need.

In the matter of intermediate nomenclature, Mr. Shreve has elected to steer a middle course between the scientific system sanctioned by *Chemical Abstracts*, and the popular or "trivial" nomenclature common to manufacturing and commercial parlance. For example, the data for 8-amino-1-naphthol-3,6-disulfonic acid are given under "H-Acid," with cross indexing under the scientific name. For technical and commercial use, this is no doubt justifiable, but may retard the adoption of that pure scientific nomenclature for which the author pleads in his introduction. In the glossary of dyestuffs of German and Swiss origin, it is unfortunate that all the current American and English marks were not included.

A careful review of the dyes listed under each intermediate reveals the fact that to each dye is assigned a "Schultz" number. The book is therefore an inverted "Schultz Tabellen." As is well known, many important commercial types are not listed in Schultz, because the composition of such dyes is a commercial secret. If any one of these "unknown" dyes had been included in the new classification by intermediates, it would have been impossible to assign a Schultz number to it. We are hence forced to conclude that Mr. Shreve's book is primarily a retabulation of Schultz data, with several valuable additions, such as the American import and manufacturing statistics, the intermediate formulas and glossary, the methods of formation of intermediates, and new literature references. Even with such limitations, the book should find a wide field of usefulness.

The book is well arranged, and both the author and the publishers are to be congratulated on the general appearance and clear typographic work.

Charles L. Reese

A Textbook of Chemical Engineering. By Edward Hart, Ph.D. xiv + 241 pp. 2nd edition. The Chemical Publishing Co., Easton, Pa., 1922. Price, $4.00.

In the preface to the first edition the author writes, "If future editions should be called for I hope****to prepare a much better treatise on the subject." The second edition has appeared and differs but little from the first. In the preface to the second edition, Dr. Hart states, "As in the first edition, I have obtained considerable information not otherwise obtainable from the manufacturers of apparatus whose names are mentioned in the text." This statement is truly indicative of much of the reading matter offered in the book.

There can be no objection to the proper use of information gleaned from manufacturers of apparatus, but there is an obvious danger in using such information in a textbook for the chemical engineering student unless the information is accompanied by a discussion of the principles involved and of the relative advantages of the different types of apparatus.

We find that Chapter I offers a net total of 15 pages on materials, including iron, steel, various ferrous and nonferrous alloys, as well as glass, silica, stoneware, cement, paints, etc. Chapter II, on corrosion, is allowed 5 pages, two of which are tables and one of which complains of the "paucity of information" and "obstacles to publication." Chapter III is entitled "Location of Works." Chapter IV totals 3 pages on industrial management. Chapters V and VI, on Boilers and Prime Movers, respectively, might well be replaced—such subjects are properly covered in mechanical engineering textbooks. Chapters VII and VIII, on plumbing and on pumps, might have been made very [illegible] the chemical engineer.

The following chapters (IX to XXI) take up successively some of the unit operations in chemical engineering practice, *viz.*, crushing, mechanical handling of materials, dissolving, filtration, tanks, evaporation, crystallization, drying, distillation, absorption of gases, mixing and kneading, autoclaves, and containers.

Of the total 241 pages of material offered in Dr. Hart's textbook, 5 are allotted to index, and 110 to cuts and illustrations mostly available in trade catalogs. The remainder of the text is, in general, descriptive, and very little attempt is made to discuss fundamentals or basic principles.

R. S. Tour

Practical Tanning. By Allen Rogers, Ph.D. 23 × 15 cm. xxvi + 699 pp., 124 figs. Henry Carey Baird Co., Inc., 28 West 45th St., New York. Price, $10.00 net.

This book is "partly based on the third edition of 'Practical Tanning' by Louis A. Flemming" and, as its title indicates, is concerned almost entirely with the practical details of the conversion of hides and skins into leather. The description of processes is full and complete, and the tanner will find a great number of recipes and formulas from which to choose. There are occasional slips, *e. g.*, roller leather is very rarely "made from lambskins;" sheep are used almost exclusively (p. 231). In quoting from English sources the author has failed to correct for the difference between the Imperial and the American gallon. Omissions which should be rectified are the recent mechanical methods in liming and the utilization of by-products.

The chemist wishing to understand the mechanism of the processes will find only the barest discussion of principles, and then often in so general terms as to be misleading. The descriptions of the formation of sodium hydroxide by electrolysis of the chloride (pp. 85 to 86) and of the theory of chrome tanning (pp. 198 to 201) are confusing, and the theory of arsenic limes is scarcely in accord with the classic research of Stiasny.

Analytical methods occupy 80 pages and comprise those in general use in this country. Some discussion of water softening should have been included and also a brief description of recent analytical methods, those of W. R. Atkin and co-workers for lime liquors, Wilson and Kern for tannin, and A. W. Thomas for free mineral acid in leather.

The book is well printed on good paper, there are only a few misprints, and the illustrations of tannery processes are refreshingly modern.

F. L. Seymour-Jones

Modern Gas Works Practice. By Alwyne Meade. 815 pp. Published by Benn Brothers, Ltd., London, 1921. Price, 55s. net.

The second edition of this excellent English review of the gas art is considerably larger than the first. Chapters on high temperature measurement, naphthalene, and the complete gasification of coal have been added.

The portions of the book devoted to coal gas have received the greatest attention and the detailed descriptions of the various modern types of carbonizing plant should prove extremely valuable to all gas engineers. The chapter on the complete gasification of coal is the first concise review of a problem that promises to be of greater importance in the near future.

The author has added a considerable number of literature references that were entirely lacking in the first edition. In view of the completeness of the work, it is rather curious that practically no mention is made of methods of metering the gas.

From an American viewpoint, there are a number of matters that have not been covered. The statement that "water gas must be looked upon essentially as an auxiliary to coal gas" will sound rather curious to American readers, as will the statement that "Humphrey and Glasgow developed and improved the Lowe apparatus for the manufacture of water gas."

Air meters on water-gas sets, we are told, are a luxury and the automatic control of water-gas apparatus which has been so successfully used in America has apparently not reached England.

In view of the general high standard of the work with the excellent illustrations and typographical work, these are probably minor criticisms. In general, the author is far happier in his discussion of the engineering features of the design, construction, and operation of the apparatus than in his discussion of the theoretical considerations. It is to be regretted that we have no book covering American practice in this same fashion.

W. H. Fulweiler

COMMERCE REPORTS

Notice—*Commerce Reports are received by all large libraries and may be consulted there, or single numbers can be secured by application to the Bureau of Foreign and Domestic Commerce, Department of Commerce, Washington, D. C. The regular subscription rate for these Commerce Reports mailed weekly is $3.00 per year (10 cents per single copy), payable in advance to the Superintendent of Documents, Government Printing Office, Washington, D. C.*

June

The schedule of prices for **nitrate** fixed by the Chilean Nitrate Producers Association for the year which began July 1 is considerably lower than for last year. (P. 594)

There is a slow but steady improvement in the output of **crude oil** in the Baku fields but the Grozny fields show a decrease in production. (P. 619)

There is on file at the Fuel Division of the Bureau of Foreign and Domestic Commerce a complete list of the **petroleum wells** drilled in the Panuco section of the Tampico oil district, up to September 1, 1921. (P. 620)

The production of crude and refined **petroleum** in Italy during the year 1920 was as follows: Crude petroleum, 4937 metric tons; mineral oil, 1506 metric tons; light oil, 336 tons; refined petroleum, 1435 tons; gasoline, 1563 tons; naphthalene, 15 tons. (P. 620)

The report comes from Afghanistan that some very important **petroleum** deposits have been discovered there. (P. 620)

In order to expedite customs clearance in Egypt shippers of **varnish** containing alcohol are requested to indicate clearly in the invoices the percentage of alcoholic content in the varnish; whether or not the alcoholic content is denatured, and, if so, the character and percentage of each denaturant. (P. 641)

The existence of **petrol** in the Lake Albert region of Africa has been reported. (P. 670)

It is reported that **oil** has been struck on the government boring at D'Arcy, near Dulkeith, in Scotland, and that there is prospect of a considerable production. (P. 670)

Selling prices on **gasoline** and **kerosene** in Pernambuco have been driven down below cost by reason of competition between large importing companies. (P. 670)

According to a recent Egyptian decree, the former provision allowing exemption from excise duty on **alcohol** exclusively destined for scientific, medical, or pharmaceutical use at the discretion of the Minister of Finance, is abolished. (P. 710)

According to a Swedish royal decree dated April 21, effective April 23, 1922, an import duty of 2 crowns per kilo is levied on **bleached artificial silk** other than that put up in small retail packages for retail sale. Bleached artificial silk, formerly admitted free of duty, is now dutiable at the same rate as dyed artificial silk. (P. 711)

The Bureau of Foreign and Domestic Commerce has received a translation of the recent law pertaining to the registration of **patents, designs, industrial models,** and **trade-marks** in Jugoslavia. (P. 713)

Extensive deposits of **rock phosphate** are believed to be available on the Island of Panay, Philippine Islands. Accessible supplies of phosphate would be of great value to the Philippine sugar industry, and the Bureau of Science has started investigation along this line. (P. 721)

A new process for cleaning **kauri gum** has been devised in New Zealand which produces a product 98 per cent pure as against 80 to 85 per cent in other processes. It is estimated that this new process will cut the cost $15 per ton. (P. 721)

There is an opportunity for the United States to profit by the Japanese demand for **paraffin** and **stearin,** provided American manufacturers and exporters are able to meet the prices placed upon their products by manufacturers in Burma, Sumatra, and Australia. (P. 721)

The **fertilizer** industry and market in South Africa are reviewed (Pp. 723–4)

The **petroleum** trade and industry of Czechoslovakia are described. Apparently, the participation of American companies in the Czechoslovakian oil trade in the future will depend upon their ability to compete in price with similar products from neighboring countries. (P. 736)

Opportunities for American exporters of refined **paraffin wax** and **stearin** in western Greece seem to be improving. (P. 738)

The hold on the **artificial leather** market of Chile which American exporters gained during the World War is fast disappearing before the influx of a superior product from Great Britain. (Pp. 757–8)

Every effort is being made in France to discover new material with which to manufacture **paper pulp,** and with this in view a new company has been organized for the purpose of producing paper pulp from plants and especially from esparto or alfa grass. (P. 765)

A company in Brazil is preparing to produce paper from straw and paraná pine and will manufacture **chemical wood pulp** for the purpose. This is said to be the first concern in South America to produce chemical wood pulp for paper making. (P. 765)

The Chilean **nitrate** prices, quoted on metric quintals, are given for the coming year. (P. 787)

Statistics are given showing the average monthly **wages** of technical men and office workers in the German chemical industry in 1921. (Pp. 793–4)

The French **heavy chemicals** industry is improving with business much better than a year ago and prices well maintained. Chemicals for tanning, glassworks, and paints, however, still remain inactive. Synthetic products for drugs and perfumes are satisfactory. (P. 801)

In the Belgian chemical industry **sulfuric** acid plants are fully occupied with the demand from fertilizer manufacturers, especially German, but overproduction of **hydrochloric** acid is resulting in lower prices. (P. 803)

Statistics are given showing the production of precious and base **metals** in Mexico for the last three calendar years. (P. 827)

The Spanish **iron-ore** district is facing the most serious industrial depression experienced for many years. (P. 827)

The Bureau of Foreign and Domestic Commerce has on file detailed information relative to a large **mica** deposit in Argentina which the owner is desirous of selling. Arrangements to see samples of the mica may be made through the Bureau. (P. 828)

Statistics are given showing the production of **olive oil** in Italy for the 1909–1920 period. (P. 833)

There are in course of construction in central Italy six plants for the production of **electrical** and **mechanical energy** which will utilize nationally produced combustibles. (P. 837)

Experiments in the use of **turf** and **peat** as fuel in Finland have demonstrated that these products have apparently little chance to replace wood as the almost universal fuel in Finland. The two principal barriers to the success of the turf-fuel industry are high prices and the difficulty of securing a fuel which is sufficiently dry to permit proper combustion. (Pp. 837–8)

A Swedish engineer is reported to have worked out a method whereby a very cheap **fuel** can be obtained from the residue or lye which results from the manufacture of cellulose. By this method, it is reported, an annual production of about 100,000 tons of cellulose will result in the production of about 800,000 tons of the new fuel. (P. 838)

A good market is reported in Wales for **lubricating** and **paint oils.** (P. 840)

France has increased her import duty on **lead.** (P. 857)

The present duty on **vanadium** exported from Peru will be continued throughout 1922. (P. 859)

The production of Sicilian **sulfur** in 1921 amounted to 240,049 tons and the exportation amounted to only 105,063 tons. (P. 860)

The Russian **mining** industry in 1921 and the first quarter of 1922 is reviewed. (Pp. 862–3)

SPECIAL SUPPLEMENTS ISSUED

ARGENTINA
CANADA
CHINA
THE NETHERLANDS
UNITED KINGDOM

CURRENT PUBLICATIONS

NEW BOOKS

Applied Chemistry. [illegible] N. Peters. 461 pp. Illustrated. Price, [illegible], St Louis Mo.

Bibliography of Periodical Publications on Paper-Making and Allied Subjects during 1921. 37 pp. Price, 5s. Published by Papermakers' [illegible] Great Britain and Ireland, London.

Boiler-Plant Testing. David Brownlie. 168 pp. Price, 10s. 6d. Chapman & Hall, Ltd., London.

Catalysis with Special Reference to Newer Theories of Chemical Action. A General Discussion held by the Faraday Society. 675 pp. Price, 9s. The Faraday Society, London.

Chemical Technology and Analysis of Oils, Fats and Waxes. J. Lewkowitsch. 6th edition, entirely revised. Vol. II. 959 pp. Illustrated. Price, [illegible] The Macmillan Co., New York.

Chemistry and Its Uses: a Textbook for Secondary Schools. William McPherson and William Edwards Henderson. 447 pp. Illustrated. Price, $1.60. Ginn & Co., Boston.

Chemistry: Cours de Chimie (Métaux et Cations). Marcel Boll and Georges [illegible]. 352 pp. Illustrated. Price, 26 fr. Dunod, Paris.

Dyes: Les Matières Colorantes de Synthèse et les Produits Intermédiaires Servant à leur Fabrication. John Cannell Cain and Jocelyn Field Thorpe. Translated from the fourth English edition by G. Delmarcel and M. Drapier. 640 pp. Price, 58 fr. Dunod, Paris.

Electrically Conducting Systems: The Properties of Electrically Conducting Systems. Charles A. Kraus. American Chemical Society Monograph Series. 415 pp. Illustrated. Price, $4.50. The Chemical Catalog Co., Inc., New York.

Fertilizers: Statistique des Engrais et Produits Chimiques Destinés à l'Agriculture. Vol. II, 1910–1920. Preface by M. L. Aguillon. Price, 35 fr. Bureau d'Études Economiques Industrielles et Agricoles, Paris.

Industrial Nitrogen. P. H. S. Kemp. 100 pp. Price, 2s. 6d. Sir Isaac Pitman & Sons, Ltd., London.

Industrial Year Book, 1922. 1086 pp. Price, 36s. net. Philip Gee, London.

Inorganic Chemistry: Cours de Chimie Inorganique. Fred Swartz. 3rd edition, revised and enlarged. 418 pp. Price, 50 fr. Dunod, Paris.

Laboratory Exercises in Inorganic Chemistry. James F. Norris and Kenneth L. Mark. International Chemical Series. 548 pp. Price, $2.00. McGraw-Hill Book Co., Inc., New York.

Mathematical Theory of Probabilities and Its Application to Frequency Curves and Statistical Methods. Vol. I—Mathematical Probabilities, Frequency Curves, Homograde and Heterograde Statistics. Arne Fisher. Translated from the Danish by Charlotte Dickson and William Bonynge. 2nd edition, enlarged. 289 pp. Price, $5.00. The Macmillan Co., New York.

Minerals: Technologie des Minerals Complexes Ateliers Modernes de Préparation Mécanique des Minerals. J. Roux Brahic. 896 pp. Illustrated. Price, [illegible] fr. Dunod, Paris.

Modern Chemistry, Pure and Applied. A Treatise Dealing with All Branches of Chemistry—Mineral, Metallurgical, Organic, Pharmaceutical, and Industrial. Arthur J. Hale. Vol. IV. 287 pp. Illustrated. Price, [illegible] D. Van Nostrand Co., New York.

Optical Instruments: The Theory of Modern Optical Instruments; a Reference Book for Physicists, Manufacturers of Optical Instruments and for Officers in the Army and Navy. Alexander Gleichen. Translated by Emsley and Swain. 365 pp. Illustrated. Price, $4.00. [illegible] New York.

Organic Chemistry: Theoretical Organic Chemistry. Julius B. Cohen. 2nd edition, reprinted. 604 pp. Price, $2.60. The Macmillan Co., New York.

Paint: How to Paint Permanent Pictures. Maximilian Toch. 105 pp. Price, $1.25. D. Van Nostrand Co., New York.

Paper: Die Chemische Betriebskontrolle in der Zellstoff- und Papier-Industrie [illegible] 2nd edition. 474 pp. Illustrated. Price, $5.40. Julius Springer, Berlin.

Qualitative Analysis: Course of Instruction in the Qualitative Chemical Analysis [illegible] 9th edition. [illegible] New York.

Qualitative Analysis: Supplement to Notes on Qualitative Analysis. H. J. H. [illegible] Cambridge, England.

Quantitative Analysis: Leitfaden der Quantitativen Analyse. F. Hahn. 230 pp. Price, paper, 6s.; bound, 7s. 2d. Theodor Steinkopff, Dresden and Leipzig.

Quantum Theory: Fortschritte der Quantentheorie. A. Landé. **Wissenschaftliche Forschungsberichte.** Vol. 5. 91 pp. Price, 3s. 6d. Theodor Steinkopff, Dresden and Leipzig.

Radioactive Substances: An Introduction to the Chemistry of Radioactive Substances. A. S. Russell. 173 pp. Price, $2.00. The Macmillan Co., New York.

Vitamins and the Choice of Food. Violet G. Plimmer and R. H. A. Plimmer. 164 pp. Price, 7s. 6d. Longmans, Green & Co., London.

Vitamins: Newer Aspects of the Nutrition Problem. Frederick Gowland Hopkins. 19 pp. Price, 75 cents. Lemcke & Buechner, New York.

Wood: A Textbook of Wood. Herbert Stone. 247 pp. Illustrated. Price, $5.50. D. Van Nostrand Co., New York.

RECENT JOURNAL ARTICLES

Arsenic Therapy. Homer W. Smith. *Journal of the American Pharmaceutical Association*, Vol. 11 (1922), No. 6, pp. 423–32.

Catalysis and Catalytic Agents in Chemical Processes. Hugh S. Taylor. *Journal of the Franklin Institute*, Vol. 194 (1922), No. 1, pp. 1–27.

Ceramics: Physical Chemistry and Ceramics. Edward W. Washburn. *Journal of the Franklin Institute*, Vol. 193 (1922), No. 6, pp. 749–73.

Enamels: Microscopic Study of Ground Coat and Cover Coat Enamel Reactions. E. E. Geisinger. *Journal of the American Ceramic Society*, Vol. 5 (1922), No. 6, pp. 322–37.

Fuel: Relative Value of Coal and Oils as Fuels. C. H. Butz. *Forging and Heat Treating*, Vol. 8 (1922), No. 6, pp. 262–65.

Glass: An Examination and Extension of Zulkowski's Theory of the Relation between the Composition and Durability of Glasses. William Learmonth Baillie. *Journal of the Society of Glass Technology*, Vol. 6 (1922), No. 21, pp. 68–95.

Glass: The Modern Glass Factory. W. S. Mayers. *The Glass Industry*, Vol. 3 (1922), No. 7, pp. 129–34.

Glass: Solubility and Decomposition in Complex Systems. George W. Morey. *Journal of the Society of Glass Technology*, Vol. 6 (1922), No. 21, pp. 20–29.

Glue: Contributions to the Chemistry and Technology of Gelatin and Glue. Robert Herman Bogue. *Journal of the Franklin Institute*, Vol. 193 (1922), No. 6, pp. 795–825; Vol. 194 (1922), No. 1, pp. 75–82.

Heat Transmission, with Special Reference to the Stoker Fired Boiler. R. M. Howe and S. M. Phelps. *Journal of the American Ceramic Society*, Vol. 5 (1922), No. 7, pp. 420–29.

Iron: The Effect of Oxidizing Gases at Low Pressure on Heated Iron. H. C. H. Carpenter and C. F. Elam. *Blast Furnace and Steel Plant*, Vol. 10 (1922), No. 6, pp. 317–19.

Leather: The Bacteriology of Fresh Steer Hide. George D. McLaughlin and George E. Rockwell. *Journal of the American Leather Chemists Association*, Vol. 17 (1922), No. 7, pp. 325–40.

Lignite: Procédés Modernes pour le Traitement du Lignite et de ses Dérivés. Ch. Berthelot. *Chimie et Industrie*, Vol. 7 (1922), No. 5, pp. 855–63.

Metals: The Casting of Metals. Thomas Turner. *Brass World*, Vol. 18 (1922), No. 6, pp. 191–95.

Mordants. Wilder D. Bancroft. *Journal of Physical Chemistry*, Vol. 26 (1922), No. 5, pp. 447–70; No. 6, pp. 501–36.

Nutrition: L'Alimentation dans ses Rapports avec le Besoin Qualitatif d' Azote (Amino-Acides Indispensables) et les Facteurs Accessoires de la Nutrition (Vitamins). A. Blanchetière. *Chimie et Industrie*, Vol. 7 (1922), No. 5, pp. 870–78.

Porcelain: The Tensile Strength of Porcelain. F. H. Riddle and J. S. Laird. *Journal of the American Ceramic Society*, Vol. 5 (1922), No. 7, pp. 385–93.

Rubber: Sulla Peciosità della Gomma Greggia e sull'Invecchiamento della Gomma Vulcanizzata. Camillo Pelizzola. *Giornale di Chimica Industriale ed Applicata*, Vol. 4 (1922), No. 5, pp. 200–03.

Soap: Studies of the Constitution of Soap Solutions. Solutions of Sodium Palmitate, and the Effect of Excess of Palmitic Acid or Sodium Hydroxide. James William McBain, Millicent Taylor and Mary Evelyn Laing. *Journal of the Chemical Society*, Vol. 121 (1922), No. 714, pp. 621–33.

Steel: Physical Tests on High-Speed Steels. A. H. D'Arcambal. *The Iron Age*, Vol. 110 (1922), No. 1, pp. 1–5.

Steel: Properties of Arc Deposited Steel. O. H. Eschholz. *The Iron Age*, Vol. 109 (1922), No. 26, pp. 1803–05.

Tanning: Chrome Tanning, IX. The Relation between the Properties of Chrome Liquors and the Leather They Produce. Some Notes on the Mechanism of Chrome Tanning with Bibliography. Donald Burton *Journal of the Society of Leather Trades' Chemists*, Vol. 6 (1922), No. 5, pp. 157–79.

Vitamins: The Testing of Foodstuffs for Vitamins. J. C. Drummond and A. F. Watson. *The Analyst*, Vol. 47 (1922), No. 555, pp. 235–44.

GOVERNMENT PUBLICATIONS

Notice—*Publications for which price is indicated can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C. Other publications can usually be supplied from the Bureau or Department from which they originate*

Bureau of Foreign and Domestic Commerce

Vegetable Oils and Oil Materials in International Commerce. *Miscellaneous Series* **108.** 24 pp. Paper, 5 cents. 1922.

Bureau of Mines

Additions, Removals, and Changes in Permissible List of Explosives from March 15 to May 31, inclusive, 1922. S. P. Howell. *Reports of Investigations* **2362.** 2 pp. Issued June 1922.

Carbon Black: Its Manufacture, Properties and Uses. R. O. Neal and G. St. J. Perrott. *Mines Bulletin* **192.** Paper, 25 cents.

Design and Operation of a Low-Pressure Absorption Plant. W. P. Dykema and A. A. Chenoweth. *Technical Paper* **263.** 42 pp. Paper, 10 cents.

Explosives Used in April 1922. W. W. Adams. *Reports of Investigations* **2369.** 5 pp. Issued June 1922.

Helium. R. B. Moore. *Reports of Investigations* **2363.** 4 pp. Issued June 1922.

Ignition of Coal Dust by Electric Arcs. L. C. Ilsley and E. J. Gleim. *Reports of Investigations* **2365.** 7 pp. Issued June 1922.

Official Approval of Burrell Methane Indicator. L. C. Ilsley. *Reports of Investigations* **2367.** 3 pp. Issued June 1922.

Properties of Typical Crude Oils from the Producing Fields of Oklahoma. E. W. Dean, A. D. Bauer, M. B. Cooke and C. R. Bopp. *Reports of Investigations* **2364.** 2 pp. Issued June 1922.

Temperature Pressure Curves of Petroleum Products. M. B. Cooke. *Reports of Investigations* **2368.** 2 pp. Issued June 1922.

Durability of Cement Drain Tile and Concrete in Alkali Soils: Third Progress Report (1919-1920). G. M. Williams. *Technologic Paper* **214.** Paper, 10 cents.

Bureau of Standards

Durability of Sole Leather Filled with Sulfite Cellulose Extract. R. C. Bawker. *Technologic Paper* **215.** Paper, 5 cents.

Bureau of the Census

Phosphates: 14th Census of the United States: Mines and Quarries, 1919, Phosphate Rock. Prepared under supervision of E. F. Hartley by F. J. Katz. 10 pp. 1922.

Congress

Crude Oil and Gasoline. Resolution amending S. Res. 292, directing the Committee on Manufactures to investigate and report to the Senate the conditions of the crude oil and gasoline markets during the years 1920, 1921, and to date in 1922; agreed to April 20 (calendar day, May 15), 1922. *S. Res.* **295.** 3 pp. Introduced by Mr. LaFollette and referred to the Committee to Audit and Control the Contingent Expenses of the Senate. June 3, 1922, reported by Mr. Calder without amendment. June 5, 1922, considered and agreed to.

Muscle Shoals. A bill authorizing the acceptance of the proposal of Henry Ford for the completion and leasing of the dams and hydroelectric plants at Muscle Shoals, and for the purchase of Nitrate Plant No. 1, Nitrate Plant No. 2, the Waco Quarry, and the interest of the Government in the Gorgas Warrior River steam plant, all in the State of Alabama, dated May 31, 1922. Introduced by Mr. Ladd July 8, 1922, and referred to the Committee on Agriculture and Forestry. *S.* **3802.** 21 pp.

Oil and Gas. A bill to authorize the Secretary of the Interior to grant permits or leases to certain persons and corporations for lands and oil and gas deposits south of the medial line of the main channel of Red River, Oklahoma. Introduced by Mr. Sinnott June 30, 1922, and referred to the Committee on Public Lands. *H. R.* **12233.** 4 pp.

Reparation Commission. Resolution requesting the Secretary of State to report to the Senate the names of official or unofficial representatives of the State Department accredited to the Reparation Commission, and particulars as to their employment and sources of pay. Introduced by Mr. King, June 22, 1922, and referred to the Committee on Foreign Relations. *S. Res.* **309.** 2 pp.

Reparation Dyes. Resolution relative to the purchase and importation of reparation dyes for sale in the United States. Introduced by Mr. King July 1, 1922, and ordered to lie on the table. *S. Res.* **317.** 4 pp.

Tariff Bill. Views of minority to accompany H. R. 7456 (to provide revenue, to regulate commerce with foreign countries, to encourage industries of the United States, and for other purposes). Submitted by Mr. Simmons May 6, 1922. *S. R.* **595,** page 2. 12 pp

Water Pollution. Preventing pollution of navigable waters by oil-burning and oil-carrying steamers, report to accompany H. J. Res. 297. Submitted by Mr. Porter May 1, 1922. *H. Rp.* **950.** 2 pp.

Congressional Committees

Mining Laws. To revise, amend, and codify laws relating to location of mining claims on public domain, and for other purposes, hearings on *H. R.* 7736, April 27, 1922. Part 1. 29 pp.

Muscle Shoals. Hearings before the Committee on Agriculture and Forestry, United States Senate on S. 3420 to provide for the manufacture of explosives for the use of the Army and Navy, to provide for the manufacture of fertilizer for agricultural purposes, to incorporate the Federal Chemical Corporation, and for other purposes; and on the Henry Ford Muscle Shoals offer; offer made by the Alabama Power Co., proposing to complete Wilson Dam; offer of Frederick E. Engstrum for Muscle Shoals; and offer of Charles L. Parsons for properties at Muscle Shoals, Ala.

Part 1—February 16, April 10, 12, and 13, 1922. 96 pp.
Part 2—April 14 to May 3, 1922. 219 pp.
Part 3—May 4 to May 11, 1922. 286 pp.

Naval Petroleum Reserves. Granting oil reserve revenues to States, hearing on H. R. 11363, granting portion of rents, royalties, and bonuses received from lands within naval petroleum reserves to States within boundaries of which said reserves are located. May 9, 1922. 12 pp.

Tariff. Hearings on proposed tariff act of 1921 (H. R. 7456), statement of H. E. Miles, Chairman Fair Tariff League, for just tariff, adequately but not excessively protecting American industry and labor, miracle of American production, 29 industries analyzed, burden of excessive rates, wages, agriculture, foreign trade, American valuation, January 23, 1922. 61 pp.

Department of Agriculture

Principles of Liming Soils. E. C. Shorey. *Farmers' Bulletin* **921.** Reprint. 30 pp. Paper, 5 cents.

Geological Survey

Abrasive Materials in 1921. L. M. Beach and A. T. Coons. Separate from Mineral Resources of the United States, 1921, Part II. 4 pp. Published June 15, 1922.

Gold, Silver, Copper, Lead, and Zinc in New Mexico and Texas in 1920. C. W. Henderson. Mines Report. Separate from Mineral Resources of the United States, 1920, Part I. 15 pp. Published June 12, 1922.

Lead in 1921. General Report. C. E. Siebenthal and A. Stoll. Separate from Mineral Resources of the United States, 1921, Part I. 9 pp. Published July 3, 1922.

Magnesium in 1921. G. F. Loughlin. Separate from Mineral Resources of the United States, 1921. 2 pp. Published June 14, 1922.

Silica in 1921. L. M. Beach. Separate from Mineral Resources of the United States, 1921, Part II. 2 pp. Published June 16, 1922.

Strontium in 1921. G. W. Stose. Separate from Mineral Resources of the United States, 1921, Part II. 2 pp. Published July 5, 1922.

Sulfur, Pyrites, and Sulfuric Acid in 1920. P. S. Smith. Separate from Mineral Resources of the United States, 1920, Part II. 8 pp. Published June 16, 1922.

Zinc in 1921. C. E. Siebenthal and A. Stoll. Separate from Mineral Resources of the United States, 1921, Part I. 13 pp. Published June 17, 1922.

Public Health Service

A Physiological Test for the Activity of Vitamin Preparations. A. Seidell. *Public Health Reports*, **37** (June 23, 1922), 1519–23.

Determination of Hydrogen-Ion Concentration. F. H. McCrudden. *Reprint* **730** *from Public Health Reports.* 16 pp. Paper, 5 cents.

Improved Method for Preparation of Vitamin-Activated Fuller's Earth. A. Seidell. *Reprint* **738** *from Public Health Reports.* 2 pp. Paper, 5 cents.

Preparation of Chaulmoogra Oil Derivatives for the Treatment of Leprosy. A. L. Dean and Richard Wrenshall. *Public Health Reports*, **37** (June 9, 1922), 1395–9.

Some Conclusions Drawn from a Survey of Sewage Treatment Plants. H. H. Wagenhals. *Public Health Reports*, **37** (June 23, 1922), 1505–18.

MARKET REPORT—JULY, 1922

[SUPPLIED BY DRUG & CHEMICAL MARKETS]

Market conditions for inorganic chemicals have shown little real change during the past month. Prices have remained at approximately the same levels and business has shown a regular improvement in the basic commodities in spite of speculative movements in a few items. Consumers are gradually showing greater confidence and are even inclined to anticipate their needs in view of the low prices generally named and the belief, which is gaining ground, that advances will be in order when the fall business increase comes.

In contrast to this situation is that of the organic manufacturers. Early July found business for them on the increase. Price cutters had been largely forced out of the market on leading items, and consumers were showing an inclination to buy on the improved condition of the textile industry in New England. However, the announcement of the Department of Justice's action against the Chemical Foundation, and indirectly against the entire American dye industry, offset the basic soundness of the situation to a great extent and tended to destroy the returning confidence of consumers. When this was followed on the 15th by the refusal of the Senate to include the dye licensing provisions in the Tariff Bill, many consumers cancelled their orders or reduced them to a minimum in order to protect themselves should imported dyes become available in quantity in the near future.

Manufacturers' prices generally have shown little change. Acetate of lime was advanced by makers late in June, but the makers of acetic acid, whose price is based entirely on acetate, did not receive official notice of the advance until some time later. The present price of acetate is 2 cents per pound and that of 28 per cent acetic acid based on this figure $2^3/_8$ cents in car lots of barrels at makers' works. Makers of barium chloride are offering freely at $85 per ton in car lots f. o. b. their works. Copper sulfate has become increasingly scarce as the season advanced and makers have been unable to offer any considerable quantities for many weeks. Prices nominally quoted are around 7 cents per pound.

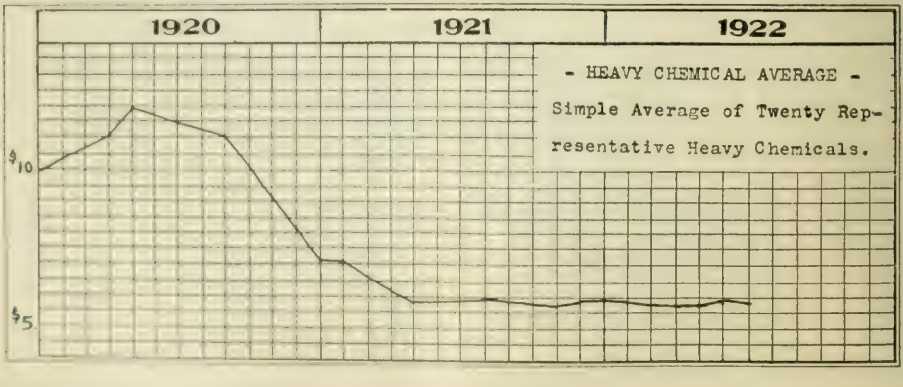
Speculative interest has been attracted to arsenic and sal ammoniac, and many firms are taking on supplies now for delivery in the late fall. Yellow prussiates of soda and potash have declined during the month in the hands of speculative buyers who were unwilling to carry stocks until such a time as the basic soundness of conditions on both items might provide satisfactory outlets. Imported barium chloride has been in much the same position with speculative holders very nervous as to the future. The slump in German marks early in July added to the uncertainty of the speculator's position and forced many holders of imported stocks to part with them on unfavorable terms.

Stocks of cheap denatured alcohol which have done much in recent months to hamper legitimate trade have been virtually wiped out and prices are correspondingly firmer at 31 cents per gallon. Acetone was advanced by makers to 10 cents per pound along with acetate of lime. Camphor has become firmer and is quoted higher. Manufacturers reduced chloroform sharply late in June. The sale of a large lot of imported hydroquinol, which had been held by the importer for more than a year, to a manufacturer, started a competitive price war and forced prices down to 80 cents on a weak basis. During the month several inquiries came into the market from Japan for glycerol in lots amounting to several thousand tons. However, the better prices offered by English makers finally took the business there.

Cottonseed oil slumped badly on the decline in German exchange early in July. Large orders had been booked by American dealers for export to Germany and stocks here had been reduced to a comfortable minimum when it became necessary for the German buyers to cancel their obligations. This threw a large lot of oil into the market here without immediate outlet and forced prices down precipitately on the New York Produce Exchange in a session of heavy selling.

Paint oils have passed their active season and are extremely dull at present. Linseed oil is held up by the firmness of flaxseed and the bullish reports from the present crop, but, lacking such a prop, China wood oil has weakened considerably here although holding fairly well in primary markets.

Animal oils have tended to advance and are much firmer in makers' hands. Fish oils are moving well and reports from fishing centers indicate a good catch for the present season in spite of the low yields per thousand fish noted by the crushers of menhaden.



Courtesy of Drug & Chemical Markets

FIRST-HAND PRICES FOR GOODS IN ORIGINAL PACKAGES PREVAILING IN THE NEW YORK MARKET

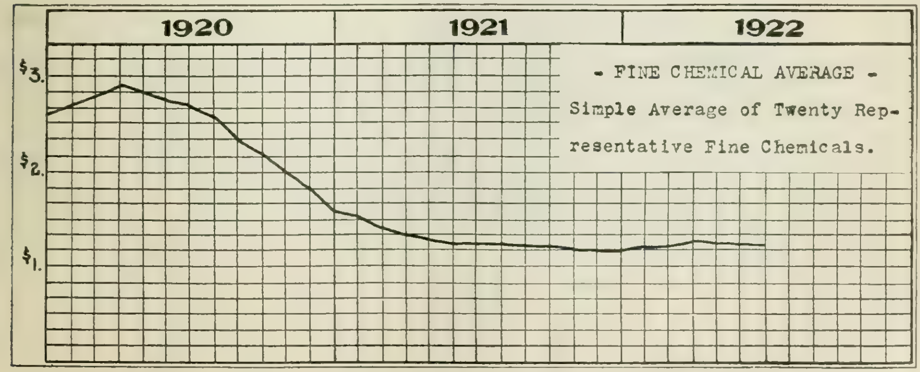
INORGANIC CHEMICALS

	July 1	July 15	Jan. 1922
Acid, Boric, cryst. bbls.......lb.	.11¾	.11¾	.12¾
Hydrochloric, comm'l. 20° lb.	.01¼	.01¼	.01¼
Hydrofluoric, 30% bbls..lb.	.07	.07	.07
Hydriodic, sp. gr. 1.150...lb.	2.25	2.25	2.00
Nitric, 42°, cbys. c/l wks.lb.	.06	.06	.06
Phosphoric, 50% tech.....lb.	.08	.08	.10
Sulfuric, C. P............lb.	.07	.07	.07
66° tks. wks........ton	16.00	16.00	16.00
Oleum 20%.........ton	19.00	19.00	19.00
Alum, Ammonia, lump........lb.	.03½	.03½	.03½
Potash, lump............lb.	*.03	*.03	*.03½
Chrome.............lb.	.06½	.06½	.07
Soda, ground............lb.	.03½	.03½	.03½
Aluminium Sulfate (iron-free).lb.	.02½	.02½	.02½
Ammonium Carbonate, pwd...lb.	.07	.07	.08
Chloride, white gran......lb.	.07¾	.07¾	.07½
Ammonia, anhydrous ....lb.	.30	.30	.30
Ammonia Water, drums, 26°...lb.	.07½	.07½	.07½
Arsenic, white...............lb.	.07¼	.07¼	.06½
Barium Chloride............ton	*95.00	*90.00	*53.00
Nitrate.................lb.	*.06	*.06	*.07
Barytes, white..............ton	33.50	33.50	28.00
Bleaching Powd., 35%, works ....100 lbs.	1.60	1.60	2.25
Borax, cryst., bbls...........lb.	.05½	.05½	.05¾
Bromine, pure, wks...........lb.	.23	.23	.23
Calcium Chloride, fused, f.o.b. N. Y....................ton	24.50	24.50	28.75
Chlorine, liquid..............lb.	.06	.06	.06
Copper Sulfate..........100 lbs.	6.50	7.00	5.55
Iodine, resublimed...........lb.	4.20	4.20	3.80
Lead Acetate, white crystals...lb.	.10½	.10½	.11
Nitrate.................lb.	.15	.15	.15
Red....................lb.	.08	.08	.08
White (Carb.)............lb.	.07¼	.07¼	.07¼
Lime Acetate...........100 lbs.	2.00	2.00	1.75
Magnesium Carbonate, tech...lb.	.06	.06	.06
Magnesite, calcined..........ton	55.00	55.00	55.00
Phosphorus, yellow...........lb.	*.25	*.25	*.27
Red....................lb.	*.26	*.26	*.30
Plaster of Paris.............bbl.	4.25	4.25	4.25
Potassium Bichromate........lb.	.09¾	.09¾	.10½
Bromide, imported.......lb.	*.15	*.15	*.13
Carbonate, calc., 80-85%.lb.	*.04¾	*.04¾	*.04½
Chlorate, cryst...........lb.	*.06½	*.06½	*.05½
Hydroxide, 88-92%......lb.	*.05½	*.05½	*.06
Iodide, bulk.............lb.	3.30	3.30	2.90
Nitrate.................lb.	.08	.07	.08
Permanganate, U. S. P....lb.	*.14	*.14	*.15
Prussiate, red............lb.	*.90	*.90	*.29
Yellow..............lb.	*.31½	*.30½	*.24½
Salt Cake, bulk.............ton	21.00	21.00	17.00
Silver Nitrate................oz.	.48	.48	.44½
Soda Ash, 58%, bags.....100 lbs.	*1.80	*1.80	*1.85
Caustic, 76%, N. Y..100 lbs.	3.75	3.75	3.80
Sodium Acetate..............lb.	.05	.05	.04
Bicarbonate.........100 lbs.	2.00	2.00	2.00
Bichromate..............lb.	.07¼	.07¼	.07¾
Bisulfite, powd...........lb.	.04¼	.04¼	.04¼
Chlorate.................lb.	.06¾	.06¾	.07½
Cyanide, 96-98%........lb.	.24	.23	.28
Fluoride, tech............lb.	.09½	.09½	.09½
Hyposulfite, bbls.....100 lbs.	3.25	3.25	3.50
Nitrate, 95%........100 lbs.	2.55	2.55	2.32½
Nitrite..................lb.	.09½	.09½	.06½
Prussiate, yellow.........lb.	.22	.21½	.16½
Phosphate (di-sod.),tech..lb.	.04	.04	.04¼
Silicate, 40°.............lb.	.01	.01	.01⅛
Sulfide, 60%, fused.......lb.	.04	.04	.05
Strontium Nitrate............lb.	*.08	*.08	*.10
Sulfur, flowers...........100 lbs.	3.00	3.00	2.75
Crude, mines.......long ton	14.00	14.00	16.00
Tin Bichloride, 50% sol'n......lb.	.10½	.10½	.09¼
Oxide...................lb.	.38	.38	.37
Zinc Chloride, U. S. P.........lb.	.35	.35	.35
Oxide, bbls..............lb.	.08	.08	.08

*Resale or Imported (not an American makers' price).

ORGANIC CHEMICALS

	July 1	July 15	Jan. 1922
Acetanilide, U. S. P. bbls.......lb.	*.29	*.29	*.29
Acid, Acetic, 28 p. c.......100 lbs.	2.37½	2.37½	2.37½
Glacial..............lb.	.08	.08	10
Benzoic, U. S. P........lb.	.55	.55	.60
Carbolic, cryst., U. S. P., drs...............lb.	.14	.14	.12
50- to 110-lb. tins....lb.	.21	.21	.18
Citric, crystals, kegs......lb.	*.44½	*.44½	*.43
Oxalic, cryst., bbls., wks...lb.	.11½	.11½	.14
Pyrogallic, resublimed....lb.	1.60	1.60	1.75
Salicylic, U. S. P.........lb.	.26	.26	.24
Tannic, U. S. P., bbls....lb.	.70	.70	.75
Tartaric, cryst., U. S. P...lb.	*.28½	*.28½	*.25
Acetone, drums..............lb.	.10	.10	.12
Alcohol, denatured, complete.gal.	.31	.31	.45
Ethyl, 190 proof, bbls....gal.	4.65	4.65	4.75
Amyl Acetate................gal.	1.90	1 90	2.00
Camphor, Jap, refined, cases...lb.	.78	.80	.90
Carbon Bisulfide, c/l.........lb.	.06	.06	.06½
Tetrachloride............lb.	.10	.10	.10½
Chloroform, U. S. P., drums...lb.	.25	.25	.43
Creosote, U. S. P.............lb.	.40	.40	.40
Cresol, U. S. P...............lb.	.14	.14	.14
Dextrin, corn...........100 lbs.	2.99	2.99	2.70
Imported Potato.........lb.	.09	.09	.06½
Ether, U. S. P., 100 lbs.........lb.	.14	.14	.14
Formaldehyde, bbls...........lb.	.08	.08	.10½
Glycerol, dynamite, drums....lb.	.12½	.12½	.14½
Methanol, pure, bbls.........gal.	.72	.72	.75
Methylene Blue, med.........lb.	3.00	3.00	4.00
Petrolatum, light amber......lb.	.04½	.04½	.05¼
Pyridine......................gal.	1.75	1.75	1.75
Starch, corn, pow'd......100 lbs.	2.32	2.32	2.13
Potato, Jap..............lb.	.07	.07	.06½
Sago.....................lb.	.03½	.03½	.04



Courtesy of Drug & Chemical Markets

OILS, WAXES, ETC.

	July 1	July 15	Jan. 1922
Beeswax, white ... lb.	.40	.40	.33
Castor Oil, No. 3 ... lb.	.11	.11	.10½
Ceresin, yellow ... lb.	.08	.08	.07½
Corn Oil, crude, tanks, mills ... lb.	.09½	.09½	.06¾
Cottonseed Oil, crude, f. o. b. mill ... lb.	[illegible]	.07	.07
Linseed Oil, raw car lots ... gal.	.89	.89	.69
Menhaden Oil, crude, mills...gal.	.38	.38	.35
Neat's-foot Oil, 20°..........lb	.20	.20	.16¾
Paraffin, 128–130 m. p., ref.....lb.	.03¾	.03¾	.05
Rosin, "F" grade, 280 lbs....bbl.	6.20	6.05	5.30
Rosin Oil, first run..........gal.	.36	.36	.36
Shellac, T. N. ... lb.	.78	.78	.66
Sperm Oil, bleached winter, 38° ... gal.	1.59	1.59	1.70
Stearic Acid, double pressed...lb.	.09½	.09½	.09¾
Tallow Oil, acidless...........lb.	.10	.10	.10
Turpentine, spirits of ... gal.	1.30	1.18	.82½

METALS

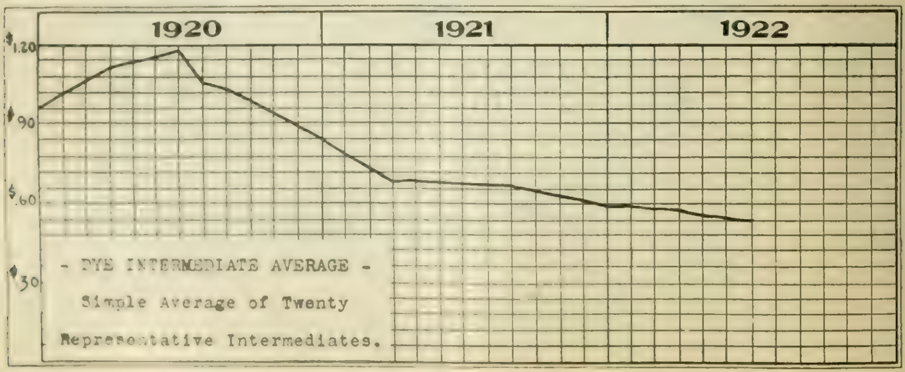
	July 1	July 15	Jan. 1922
Aluminium, No. 1, ingots.....lb.	.17½	.17½	.17
Antimony, ordinary......100 lbs.	5.25	5.00	4.55
Bismuth ... lb.	2.10	2.10	1.80
Copper, electrolytic ... lb.	.13⅞	.13⅞	.13⅞
Lake ... lb.	.13⅞	.13⅞	.13¾
Lead, N. Y..............100 lbs.	5.75	5.70	4.70
Nickel, electrolytic...........lb.	.39	.39	.45
Platinum refined, soft.........oz.	85.00	87.00	78.00
Quicksilver, flask......75 lbs. ea.	55.00	55.00	52.00
Silver, foreign ....oz.	.71⅜	.71⅜	.65¼
Tin.................lb.	.31	.31⅜	.32¾
Tungsten Wolframite ...per unit	2.00	2.00	2.00
Zinc, N. Y..............100 lbs.	5.65	5.85	5.20

FERTILIZER MATERIALS

	July 1	July 15	Jan. 1922
Ammonium Sulfate, expt 100 lbs	3.50	3.50	2.60
Blood, dried, f. o. b. N. Y....unit	3.65	3.65	3.50
Bone, 3 and 50, ground, raw..ton	28.00	28.00	30.00
Calcium Cyanamide, unit of ammonia ...	2.25	2.25	2.25
Fish Scrap, dried, wks......unit	3.50 & .10	3.50 & .10	3.25 & .10
Phosphate Rock, f. o. b. mine:			
Florida Pebble, 68%.....ton	3.00	3.00	5.00
Tennessee, 78–80%......ton	6.00	6.00	8.00
Potassium Muriate, 80%....unit	.60	.60	*.75
Tankage, high-grade, f. o. b. Chicago... unit	3.65 & .10	3.65 & .10	3.00 & .10

COAL-TAR CHEMICALS

	July 1	July 15	Jan. 1922
Crudes			
Anthracene, 80–85%.........lb.	.75	.75	.75
Benzene, pure, tanks ....gal.	.30	.30	.29
Naphthalene, flake...........lb.	.06½	.06½	.07½
Phenol, drums ... lb.	.14	.14	.11
Crudes (*concluded*)			
Toluene, pure, tanks.........gal.	.30	.30	.30
Xylene, 2 deg. dist. range, tanks..................gal.	.45	.45	.45
Intermediates			
Acids			
Anthranilic..............lb.	1.10	1.10	1.10
Benzoic, tech............lb.	.50	.50	.50
Cleve's..................lb	1.50	1.50	1.50
Gamma..................lb	1.80	1.80	2.25
H.......................lb.	.75	.75	1.00
Metanilic...............lb.	1.00	1.00	1.60
Monosulfonic F..........lb.	2.30	2.30	2.30
Naphthionic, crude.......lb.	.60	.60	.65
Nevile & Winther's.......lb.	1.20	1.20	1.30
Picric...................lb.	.20	.20	.25
Sulfanilic...............lb.	.22	.22	.26
Tobias'..................lb.	1.50	1.50	2.00
Aminoazobenzene............lb.	1.15	1.15	1.15
Aniline Oil..................lb.	.14	.14	.17
Aniline Salt.................lb.	.20	.20	.25
Anthraquinone (sublimed)....lb.	1.35	1.35	1.50
Benzaldehyde, tech...........lb.	.65	.65	.45
U. S. P..................lb.	1.40	1.40	1.25
Benzidine Base ....lb.	.85	.85	.90
Benzidine Sulfate............lb.	.70	.70	.70
Diaminophenol..............lb.	5.50	5.50	5.50
Dianisidine..................lb.	4.50	4.50	4.75
p-Dichlorobenzene...........lb.	.17	.17	.15
Diethylaniline...............lb.	.60	.60	.90
Dimethylaniline..............lb.	.32	.32	.40
Dinitrobenzene...............lb.	.20	.20	.21
Dinitrotoluene...............lb.	.20	.20	.25
Diphenylamine...............lb.	.58	.58	.58
G Salt.......................lb.	.65	.65	.70
Hydroquinol..................lb.	.90	.80	1.35
Monochlorobenzene..........lb.	.10	.10	.10
Monoethylaniline............lb.	1.00	1.00	1.00
b-Naphthol, dist.............lb.	.23	.23	.30
a-Naphthylamine............lb.	.30	.30	.30
b-Naphthylamine............lb.	.95	.95	1.05
m-Nitroaniline...............lb.	.72	.72	.85
p-Nitroaniline...............lb.	.75	.75	.77
Nitrobenzene (Oil Mirbane)...lb.	.10	.10	.10
p-Nitrophenol...............lb.	.75	.75	.75
o-Nitrotoluene..............lb.	.12	.12	.15
p-Nitrotoluene..............lb.	.60	.60	.70
m-Phenylenediamine.........lb.	1.00	1.00	1.10
p-Phenylenediamine.........lb.	1.50	1.50	1.60
Phthalic Anhydride..........lb.	.35	.35	.38
R Salt.......................lb.	.55	.50	.60
Resorcinol, tech.............lb.	1.30	1.30	1.50
U. S. P..................lb.	1.75	1.75	2.00
Schaeffer's Salt. ....lb.	.60	.60	.70
Sodium Naphthionate........lb.	.60	.60	.70
Thiocarbanilide..............lb.	.35	.35	.40
Tolidine (base)..............lb.	1.15	1.15	1.20
Toluidine, mixed.............lb.	.30	.30	.30
o-Toluidine..................lb.	.16	.16	.20
p-Toluidine..................lb.	1.00	1.00	1.10
m-Toluylenediamine..........lb.	.95	.95	1.10
Xylidine.....................lb.	.42	.42	.40



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EDITORIALS

Our Progress Number

THIS ISSUE is something of an innovation for *The Journal of Industrial and Engineering Chemistry*. It is an effort to meet numerous requests from our readers for authoritative summaries which will enable those interested but not specializing in a given field to gain some knowledge of progress therein. These reviews are intended not as short cuts to information but as a stimulus, especially to our younger chemists, to read more thoroughly beyond their own specialty or even to engage upon new investigations. It is also an attempt to acquaint our younger chemists with some of those whose work is recognized as authoritative. Several articles received too late for this issue will appear in early numbers.

If you like our idea, your thanks are due not only to those who have prepared these special articles, but also to our regular contributors who have been willing to have the publication of their articles delayed in order to give precedence to these summaries. If you have any comments or criticisms to make, please write the editor, for similar numbers may appear from time to time and suggestions are wanted.

Our policy is to do whatever we can to advance the cause of chemistry, to further the interests of chemists individually and as a profession, and to assist in the establishment and development of the chemical industry. You have a part in the achievement of these purposes, and your opinions serve to guide us.

A Type of National Service

THERE ARE a number of altruistic organizations in America in a position to investigate impartially and advise the Government on programs in special fields. Officials frequently call into conference an individual from this, that, or the other part of the country, but the instances where these national groups are called upon for particular service are disappointingly few and far between. Is the fault with the Government or with the organizations?

In times of emergency, as in the Civil War when the National Academy of Sciences was chartered, the Government feels the need of every available bit of information and experience, but in times of peace actions of far-reaching importance are often taken without paying the slightest notice to those in a position to render well-considered, sound opinions.

As a rule, scientific organizations take little part in affairs which may have a political aspect, and indeed some of them refrain from participating if an industrial aspect is possible. It is another phase of the aloofness of scientific men from public affairs. They do little to command their rightful place, yet they complain at the lack of attention given them.

We do not favor scientific organizations participating in all sorts of political and industrial arguments. That would only weaken their position. But when conditions arise in which an expression of their opinion would do much to clarify the situation and to guide our public servants, it should be given. When such conditions arise we believe that bodies like the National Academy of Sciences and the National Research Council should not wait to be called upon. Experience has shown that such calls are seldom made. The fact that they are not asked does not relieve them of their duty and responsibility. They should make an independent investigation of the facts and frankly state their findings. This is particularly true where questions of public welfare, fundamental research, and the progress of science are directly or indirectly involved. The Federated American Engineering Societies, the American Institute of Chemical Engineers, the American Chemical Society, and others who are in the habit of expressing opinions after careful deliberation have lost nothing of prestige or influence by so doing.

Time and again we hear of the importance of scientific work in the life of the republic, and then too many of us go cold when we are asked to take a decisive stand in public affairs where science is involved. We need to develop an organization consciousness as well as an individual conscience.

A Commendable Experiment

THE General Electric Company has entrusted to F. M. Dorsey an experiment which is highly commendable and unique. It is an effort to promote the mutually profitable exchange of research problems and products with men in educational institutions and with other industries.

Forward-looking industrialists have pointed to the desirability of engendering more confidential relationships between the industries and our universities. Too often in our country the college man has seen nothing but a grasping spirit in industry, while industry has regarded the college professor as a somewhat irresponsible individual with little regard for business principles. Fortunately, academic men now have a greater appreciation for the work of their colleagues in industry, which has been brought about largely by the fundamental work of such industrial laboratories as the one under W. R. Whitney at Schenectady, and that directed by C. E. K. Mees at Rochester. The results of these researches have been presented through monographs, the scientific press, and publications such as the new volume of Abridged Scientific Publications of the Eastman Kodak Company.

There has developed abroad between the industrial chemist, the chemical engineer, and the pure scientist, a close relationship with financiers and executives which has contributed largely to commercial success. Many of us would like to see a similar condition brought about in America.

The AMERICAN CHEMICAL SOCIETY, through its committee on Coöperation between Industries and Universities, is contributing toward the ultimate solution of this problem.

This new plan of the General Electric Company seems to be a step in the right direction. This company has already made a name for itself in both pure and applied research. It proposes to take the researches of university men, carry them through the development stage, and determine their commercial possibilities. It also plans to suggest to these research men the problems in which it is interested and to give them many by-products from its own industrial research. A further step is an exchange of the products of research, between this company and other great industrial groups, which would appear to be an encouraging beginning in casting off the old trade secret idea. Finally, coöperative research is contemplated.

No group of scientists will watch this experiment with greater interest than the chemists; and that it may have a fair trial we owe it our sympathetic coöperation.

Determine America's Foreign Economic Policy

MANY AMERICANS probably feel that the Genoa Conference failed because the United States declined to take part in it. Others undoubtedly think we did well to stay away, although a large number believe that by our aloofness we failed in our duty as the strongest nation.

Mr. Vanderlip, who has devoted most of his time during the last two or three years to this greatest of all economic problems, has been writing on the subject for various American newspapers. He has urged action of one sort or another, pointing out the danger to America of this threatened collapse. Other individuals and groups have also studied the question. For instance, the special committee appointed by the Chicago Association of Commerce to study this question has prepared an excellent report, "What Shall Our Foreign Policy Be?," which has recently been published by that Association. We commend it to your careful consideration.

The unrelated efforts of individuals and groups indicate a pressing need. America would not go to Genoa or to The Hague. Very well. Let America consult herself. It is greatly to be regretted that Congress and other government officials have as yet been unable to offer any solution that meets with popular support. President Harding's plan for concentrating the best minds of the country upon national problems could not be better applied than here. But we believe in this case it would be better to let the best minds take the initiative.

Our idea is that interested Americans representing every industry should get together in a national convention or conference and submit their answers to the question "What shall be our foreign economic policy?" Chemists and the chemical industry have a very important interest in the question and are particularly well organized to sit in at such a meeting. In the American Chemical Society, the American Institute of Chemical Engineers, the Manufacturing Chemists Association, the Synthetic Organic Chemical Manufacturers Association, and the Chemical Equipment Association, chemists have an excellent means for the expression of their views. Other scientific societies are similarly organized—particularly the engineers. The trade bodies, such as the National Automobile Chamber of Commerce, and such associations as the National Grange and the American Farm Bureau Federation are in a position to consider this great question in orderly manner and should be represented in this conference.

The method of procedure would be as easy to work out as was that by which the recent Conference for the Limitation of Armaments was conducted. The idea is simply this: Let America, in orderly manner, get to the task of making up her mind. Let her settle upon a program of action or non-action, as the case may be, in Europe's sadly tangled affairs.

There is only one way to do such a thing, however: If committees are appointed to consider certain questions, let their findings—both of the majority and the minority—be made public. One of the most disappointing things about the Conference for the Limitation of Armaments was the failure to follow such a policy.

Unquestionably, the reëstablishment of strong governments, balanced budgets, and work devoted to the creation of new wealth would be worth much to America, and would earn for Europe the sympathetic coöperation otherwise impossible. Such a conference could not only be the means of conveying this idea to Europe, but could make suggestions and possibly aid in the work of such reëstablishment.

Productive Chemistry

IT WOULD be interesting to know how many manufacturers still look upon the chemical laboratory as nonproductive overhead. We know of one instance where the laboratory director was indignant when he learned that his department was classed in its entirety as nonproductive and was cited as one reason why such a large percentage had to be added to production costs to cover the overhead of doing business.

It is easily understood how in times of industrial depression the departments considered to be nonproductive are the first to be discontinued or curtailed. We believe that chemists and particularly the younger men should have before them the question of whether their work is really productive.

There has been a decided change in this direction during the last generation. The graduate formerly looked forward to becoming a unit in some industrial laboratory or to taking up the dignified work of a teacher. A little later, with the coming of chemical engineering courses, laboratories of applied chemistry and the like, he looked forward to taking an active part in construction and in the perfection of factory processes began to go beyond mere control. The next stage is now upon us, in which the well-trained chemist realizes that he has an excellent opportunity to become an executive, whether as superintendent of the plant, manager of the sales department, or president of the company.

What with analysis, synthesis, research, control, and consultation, chemists are beginning to recognize that they are something more than a bearded luxury or a spare tire. Nowadays, to "get by" a chemist must be a producer, or better, a productive man. Most of them are beginning to realize that they are an important part of the money-making forces in the world's work, and not wholly the spenders, and they are feeling a commensurate responsibility. If they are productive men, they must know their depths and if weakness lies therein, be ready to correct it.

International Chemistry

THE OFFICERS of our Society were empowered by a Council vote, 138 to 7, to arrange for the continuation of the *Journal of Physical Chemistry* as a joint project with our English colleagues. Upon a better understanding of the issue, dissent has disappeared and it now seems certain that the Council at Pittsburgh will unanimously approve the new venture which has already received the hearty approval of the committee of the Chemical Society (London).

Too much cannot be said in praise of the fine spirit shown by that society, whose officers met with our representative, Charles L. Parsons, on June 23, 1922, to discuss various details. Arrangements for the appointment of a joint editorial board, the election of an editor, and agreements with respect to various policies were made. The continuation of this journal of research is to be without financial liability to either society. All details will come before the Council for final confirmation.

The plan does not run counter to any of our policies regarding *The Journal of the American Chemical Society*, and the editor, A. B. Lamb, has expressed his full approval of the final plan. The editor of the *Journal of the Chemical Society* (London) is also in full accord. We are about to take an important step, not only in the publication of scientific research in the English Language, but in establishing still another bond of friendship and coöperation with our colleagues in Great Britain. It is a joint undertaking in which the American Chemical Society has a new responsibility.

Pittsburgh as a Chemical Research Center

By **William Allen Hamor**

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THE HISTORY of chemical research in the Pittsburgh district is an informative demonstration of the material value of chemistry. In fact, the science has been the industrial searchlight which illumines dark corners of manufacturing and enables technologists to see, sometimes in dim outline, but usually plainly, much that would remain hidden if they were denied its aid. And the light once used has been applied wherever necessary.

William A Hamor

There has been a live interest in chemistry in Pittsburgh ever since the days when it was a frontier town. In 1811, F. Aigster, an honorary member of the Columbian Chemical Society, of Philadelphia, delivered a series of lectures on the application of chemistry to industry, and two years later the Pittsburgh Chemical and Physiological Society, the third chemical society in the United States, was formed under the presidency of B. Troost, a well-known early scientist. A chemical firm of those days, Trevor, Pettigrew and Troost, manufactured alcohol, ether, sweet spirits of niter, nitric acid, hydrochloric acid, calomel, and "chemical preparations generally," thus implying experimental confidence and equipment.

Indeed, chemical research carried out in the Pittsburgh district has given new industries of economic importance, as several illustrations will show.

In the first place, it is of interest to mention that the manufacture of bromine was begun in the United States in 1845 by David Alter, of Freeport, Pa., in partnership with Edward and James Gillespie. Alter was a physician of investigational resourcefulness who also conducted original research in spectroscopy and devised a commercially successful process for the destructive distillation of bituminous minerals. In 1866 works for producing bromine were erected at Tarentum, Pa., and in the following year Alter secured patent protection for his retort and process of obtaining bromine and iodine from bittern. In 1887 Francis C. Phillips, then professor of chemistry in the Western University of Pennsylvania, effected technically valuable improvements in manufacturing bromine and iodine, and his process was adopted by a company operating in Allegheny.

The pioneer work of S. M. Kier, a pharmacist of Pittsburgh, in distilling crude petroleum also deserves brief notice here. Kier began about 1855 to "refine" crude oil from a Tarentum brine well, using a still which he constructed. The "light, wine-colored" distillate which first came over was found useful for illuminating purposes as "carbon oil," while the heavier product was sold for cleaning wools. Kier adopted the Downer process of refining in 1860, obtaining more satisfactory results. Unlike Silliman's classical investigation of crude petroleum, Kier's independent work was not systematic, but it gave some information on the economic value of crude oil. In 1859 there were six "coal oil" plants near Pittsburgh, but most of them were converted into petroleum refineries soon after Drake demonstrated that petroleum could be secured by drilling.

The bringing of aluminium into the rank of the cheaper metals is looked upon generally as one of the foremost metallurgical achievements of the nineteenth century, and the historian of technology classes the industrial production of aluminium alongside the invention of Bessemer steel. Charles M. Hall, a chemist, took a metallic rarity and made out of it a common metal, and made the entire human race his debtor. The commercial development of the Hall process was begun in 1888 on Smallman St., Pittsburgh, and the manufacture of aluminium became a business success at New Kensington, Pa. Since then the progress has been wonderful, and chemistry has been the pathfinder.

Another example is the discovery of silicon carbide by E. G. Acheson. Acheson first produced carborundum in March 1891, at Monongahela City, Pa., and began its manufacture in a small way. For the first six months his production amounted to about one-fourth pound per day; but the preliminary manufacturing experimentation proving encouraging, a company was organized, and in 1894 industrial operations were transferred to Niagara Falls.

And then there is radium, Pittsburgh's great gift to American medicine. The commercial production of radium preparations was begun in the United States by the Standard Chemical Co., of Pittsburgh, in 1913. This company, organized by the late J. M. Flannery, an enthusiastic supporter of scientific research, has depended upon the radiochemical ingenuity of Charles H. Viol since the inception of its activities in 1912.

Certain nationally important industries have also been richly benefited by chemical research conducted in the Pittsburgh district. It is, for example, quite difficult to recall a more far-reaching invention than that of the dry air-blast for the manufacture of iron, devised by James Gayley, a metallurgical chemist. This discovery effected a reduction of from $0.50 to $1.00 per ton in the cost of producing pig iron, besides making it possible for the ironmaster to produce, in all weathers, a metal of uniform quality. The dry air-blast was developed by Gayley between 1885 and 1904 at the Edgar Thomson and Isabella furnaces in Pittsburgh, and between 1894 and 1911 he received no less than fifteen successive patents in this country.

In the following sections of this paper the important bearing of chemical research upon the industrial and civic welfare of Pittsburgh will be considered at some length. Special attention will be given to the application of scientific investigation in specific industries.

THE IRON AND STEEL INDUSTRIES

The Pittsburgh district produces nearly 40 per cent of the country's iron and steel. In fact, the capital invested in Pittsburgh in mills, blast furnaces, and foundries amounts to over a billion dollars, and 90,000 men are employed in its steel mills.

The technically important contributions of chemistry to the iron and steel industries began with the introduction of the great pneumatic process of steel-making. The Bessemer process and the Siemens-Martin open-hearth process produced a revolution in the iron industry that afforded the chemist his first real opportunity. Prior to the days of steel, iron-making was largely an empirical art, and no manufacturer considered the estimation or control of the impurities which generally accompany the metallurgy of iron to be a vitally important matter. Of course, it was known through the operation of the puddling and crucible processes that certain elements imparted hardness and toughness, but the very important quantitative roles in the metallurgy of iron played by carbon, manganese, sulfur, phosphorus, and silicon were not understood. Original chemical researches into the methods for determining and controlling these so-called impurities forced the essentiality of chemistry upon ferrous metallurgists. Indeed, the iron blast-furnace is but the chemist's crucible on a gigantic scale, operated on chemical principles; and the application of chemistry to iron smelting has effected such wonderful transformations that to-day the chemist occupies the foreground in directing the operations in the industry. Not only has inorganic chemistry in its analytical and physical branches played a highly important part in the steel industry, but organic chemistry has also entered the field in the by-product coking of coal. Thermochemistry, electrochemistry, and metallography are the divisions of physical chemistry which have been most active in promoting the scientific development of the metallurgy of steel. Ceramics has also been of essential aid in providing information respecting refractories.

In describing the many difficulties encountered during the early operation of the Lucy furnace at 51st St., Pittsburgh, Andrew Carnegie, the great ironmaster, says in his autobiography that the undertaking "would have been postponed if we had realized its magnitude." Little furnaces could be run by rule-of-thumb and guess, but not such a monster as the Lucy. Finally he employed Fricke, a chemist, to assist the manager, and straightway "Lucy furnace became the most profitable branch of our business, because we had almost the entire monopoly of scientific management. It was years after we had taken chemistry to guide us that it was said by the proprietors of some other furnaces that they could not afford to employ a chemist. Had they known the truth then, they would have known that they could not afford to be without one."

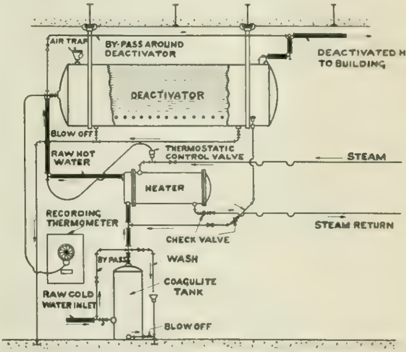
Research on Iron and Steel Products

The Carnegie Steel Company has modern analytical and control laboratories in all its plants, but it does not operate a special research laboratory. All investigations of the Central Research Bureau are carried out at the works of the company, with the facilities of the plants and the assistance of their chemical personnel. To illustrate, the laboratory of the Edgar Thomson Works is at the present time giving special research attention to refractories.

The Jones and Laughlin Steel Company follows a similar plan. This organization does not maintain a research laboratory, but chemists are detailed from the analytical laboratories of the South Side and Aliquippa Works to handle the relatively simple problems which arise in the plants from time to time.

The A. M. Byers Company's laboratory, which is located at Sixth and Bingham Sts., Pittsburgh, is engaged in the study of corrosion problems and problems incidental to the improvement of the quality of wrought iron, and in the development of processes for increased production of wrought iron, wrought-iron welded pipe being the product of manufacture. In addition to general equipment for chemical and metallographic work and for physical testing, the laboratory has special apparatus for the study of corrosion and an electric furnace and accessories for research on the production of special grades of wrought iron.

Steel tubes and pipe, seamless and welded high-pressure cylinders, and trolley poles are the principal products of manufacture of the National Tube Company, and accordingly its McKeesport laboratory is concerned especially with research on protective coatings and the control of corrosion in water where unprotected pipe is used, although mill materials and the improvement of products also receive attention. Among the accomplishments of this laboratory are a new method of finishing welded pipe without scale and with a smooth finish, non-galling steel couplings for pipe, special slow-corroding steel for pipe, and methods for the "deactivation" of water by removal of free oxygen, originally developed in 1908 and now coming into general use for the protection of pipe in hot-water lines. The laboratory has a torsion machine and a large tensile machine (600-ton) which will take a piece 30 ft. long.



Hot Water Deactivator Without Filter

▬ HEAVY LINES INDICATE COURSE OF WATER THROUGH SYSTEM
— LIGHT LINES INDICATE BY-PASSES AND OTHER NECESSARY CONNECTIONS

The research laboratory of the American Sheet and Tin Plate Co., 210 Semple St., Pittsburgh, carries out investigations of chemical engineering problems in the manufacture of sheet steel, tin plate and galvanized sheets, and studies in the metallurgy and metallography of steel, tin, and zinc, and their alloys, in pyrometry and its applications, and in the recovery of by-products. This laboratory is particularly well equipped, including precision instruments for physical testing, electric furnaces, and metallographic and pyrometric apparatus.

Vanadium, Tungsten, and Molybdenum

Vanadium, tungsten, and molybdenum and their alloys are manufactured at Bridgeville, Pa., by the Vanadium Corporation of America. Research has had and is enacting a most essential role in the success of this firm, among the accomplishments of its laboratory being a new system of electric furnace control, a process of reducing vanadium oxides by carbon in the electric furnace, producing low-carbon alloy, and the recovery of vanadium alloys from waste materials, such as slag, containing low percentages of vanadium.

The investigational work in progress includes the concentration of rare-metal ores, the electrothermal reduction of rare-metal ores, the metallography of alloy steels, and the improvement of electric-furnace regulation-control mechanisms.

Tool Steels

Research looking toward improvements in the composition and manufacture of tool and cutlery steels, and the development of better processes of heat treatment, is under way in several laboratories in the district. The Firth Sterling Steel Co., McKeesport, Pa., has a laboratory provided with experimental melting and heat-treating furnaces, testing machines, and metallographic equipment. The Vanadium-Alloys Steel Co., Latrobe, Pa., also supports a research laboratory. The Latrobe Electric Steel Company is not conducting research, although it has a works laboratory for control work.

The research achievements in the laboratory of the Crucible Steel Company of America (30th and Smallman Sts., Pittsburgh) constitute important additions to ferrous metallurgy. A number of special steels have been patented. Two more patents have been granted on a new-composition group of stain-proof, mine-water and sea-water proof, rust-proof, acid- and fire-resisting, nonmagnetic steels ("Rezistal" steels) which differ from other steels in that they require no heat treatment to bring out their resistant properties. A process has been developed for the manufacture of tungsten powder, which has been in commercial operation for ten years and has now reached a capacity of 100 tons of metallic tungsten content per month. Another development has been the business of manufacturing a special composition line of laboratory refractories, consisting of combustion boats, filtering crucibles, combustion tubes, pyrometer tubing, muffles, etc. Finally, mention should be made of the publication of a comprehensive 500-page treatise on methods of analyzing special steels, many of which procedures originated in the "Crucible Steel" laboratory.

The special laboratory equipment includes physical-testing machines, a photomicrographic outfit, experimental heat-treating furnaces, and a bottom-connected electric melting furnace with capacity and appliances for casting ingots of special alloy steels up to 400 pounds in weight.

The Crucible Steel Company of America manufactures open-hearth, crucible and electric steels, both plain carbon and alloy steels of all kinds, tungsten and molybdenum metals, plumbago crucibles, and laboratory refractories.

RADIOCHEMICAL RESEARCH

The Standard Chemical Co., of Pittsburgh, was the first commercial producer of radium in the United States (1913) and is now the world's largest producer (over 87 g. of radium produced to May 1922). It also manufactures phosphorescent zinc sulfide, luminous compounds, oxides and salts of uranium and vanadium, ferro-uranium, and ferro-vanadium.

In 1920 the Standard Chemical Company produced 18.2 g. of radium element, breaking the previous record of 13.6 g. established by itself in 1918. It required 575 men working one year to accomplish this, the quantity of ore treated amounted to 9100 tons, and the value of the finished product was $2,181,000. Seventeen grams of radium element constituted the 1921 production.

All the processes in use by this organization are the result of scientific inquiries carried out in the Vanadium Building laboratory, where [illegible] methods for the extraction of radium, uranium, and vanadium from carnotite, and in the procedures for preparing radium for therapeutic and other purposes are being sought; the metallurgical applications of uranium are also receiving study. This notable laboratory has apparatus for the analytical determination of radium and for the refining of radium salts, and photomicrographic apparatus for metallographic work.

Crystallizing Radium Barium Chlorides in the Refining of Radium Salt, Research Laboratory of the Standard Chemical Co., Pittsburgh, Pa.

RESEARCH IN THE COKE INDUSTRY

Pittsburgh is surrounded by the richest bituminous coal section of the United States and it is the cheapness of fuel which has attracted so many industries to the district. Within a radius of a few miles are more than 350 coal mines, which are capable of turning out 100,000,000 tons a year. Normally, Pittsburgh produces three-fourths of the bituminous coal in Pennsylvania and over 40 per cent of the country's output, while Connellsville, heart of the coking region and an integral part of the Pittsburgh district, alone supplies the country with 25 per cent of its coke. Fifty per cent of all the coke in the United States comes from the Pittsburgh district.

The development of the by-product oven industry in the United States was begun by the Solvay Process Co., which, in 1891, started the construction of 12 Semet-Solvay ovens in Syracuse, N. Y. The design of this type of oven had already been well established in Europe. An initial plant of Otto-Hoffmann ovens was built at Johnstown, Pa., in 1895, and began making coke in 1896. By the close of 1900 the number of completed ovens included 345 Semet-Solvay, 680 Otto-Hoffmann, and 60 Newton chambers, the latter being a modified type of beehive oven adapted with apparatus for by-product recovery, which, like all similar hybrid designs, did not long survive. Of utmost importance in the development of the by-product oven was the use of silica brick, which was first introduced in the Johnstown plant in 1899. This material was indispensable for the high temperatures, rapid coking, and high plant yields that were subsequently attained. An important improvement in by-product recovery was the system of gas separation introduced by F. Schniewind in 1899 in the plant of Otto-Hoffmann ovens at Everett, Mass.

For a number of years the progress of by-product coke making was slow, being retarded by imperfections of construction, difficulties of operation, and finally by the deep-rooted prejudice of blast-furnace men against by-product coke. In 1908, however, the industry received a marked impetus as the result of the activities of the U. S. Steel Corporation, which, after an exhaustive study of various European types of ovens and by-product apparatus, selected the Koppers design and built a 280-oven plant of this type in Joliet, Ill. This plant, which had the old indirect system of ammonia recovery, was successful beyond all expectations, and was rapidly followed by the construction of large plants using the Koppers direct process, at Gary, Ind., Fairfield, Ala., and Duluth, Minn. The European war caused an enormous increase in the construction of by-product ovens, and at present it would seem that at the close of another decade little should remain of beehive coke manufacture.

The Koppers Company designs, manufactures, and instals plants and apparatus for by-product coke and gas manufacture, concentrating ammonia liquor, ammonium sulfate recovery, benzol recovery, gasoline absorption and recovery, tar distillation, water-gas and producer-gas manufacture, and gas purification (liquid process). Its research laboratory in the Mellon Institute is excellently equipped with apparatus for coal carbonization at high and low temperatures, coal washing, coke research, gas purification by dry and liquid processes, furnaces for the investigation of refractory materials at high temperatures, laboratories and experimental plant fully equipped for semicommercial tests, and plants available for large-scale tests in relation to coke and gas manufacture and by-product recovery. Among the research accomplishments are the recovery of benzene and toluene from carburetted water-gas, the manufacture of coumarone and other resins, motor fuels, and improved blueprint, purification of ammonia-still waste, improved methods of gas purification, recovery of hydrogen sulfide, and special methods of coke investigation. Members of this organization have about 60 United States patents issued or favorably acted upon. The lines of research at present in progress are as follows: coal carbonization, gas production and purification, by-product recovery, secondary treatment of various by-products, general fuel research, refractories, pyrometry, and coal properties.

APPARATUS FOR GAS PURIFICATION BY LIQUID PROCESS (TREATING 25,000,000 CU. FT. OF GAS PER DAY) DEVELOPED BY THE KOPPERS COMPANY LABORATORIES

RESEARCH IN THE GLASS INDUSTRY

The glass industry is one of the most important in the Pittsburgh district, 62 factories producing window glass, plate glass, lighting glass, and numerous other forms of glassware. The total capital investment exceeds a quarter-billion dollars, and normally there are employed more than 25,000 workmen at a total annual payroll of over $20,000,000.

Though American contributions to the advance of the glass industry have been largely from the engineering standpoint, it is not to be supposed that the chemist and the physicist have entirely neglected this great field. In fact, the part of these scientists has been of greater importance than is usually acknowledged. Little has been written of the chemist's accomplishments, except, perhaps, in connection with the development of optical glass during the past few years. As Tillotson has indicated, chemical contributions have been isolated, sporadic, and, unfortunately, dimmed in the shadow of a general policy of secrecy which has resulted partly from tradition and partly from fear of legal complications. Such conditions do not make for real scientific progress in this or any other industry; but it is believed that the present is a period of transition, and it is certain that great opportunities exist for the chemist and that his work in the future, in conjunction with that of the physicist and engineer, will transform the whole aspect of glass technology. The problems which are to be solved include the basic principles of all the operations involved and of the materials employed. The problems in connection with refractories, furnaces, fuel and raw materials are shared in common by all branches of the glass industry.

The following important developments in glass technology have originated in the Pittsburgh district: The first regenerative pot furnace was built at the O'Hara Glass Works in 1865 by J. B. Lyon; natural gas was first used in melting glass in 1882 by the Bradford Window Glass Co., and two years later it was employed for melting flint glass at Wellsburg, W. Va.; the prepressed blank was invented by Philip Arbogast, of Pittsburgh, in 1882, and marked a fundamental step in the evolution of the automatic bottle machine; selenium ruby glass was first manufactured by Nicholas Kopp, of Pittsburgh, in 1894; flint glass was first melted in a tank furnace by C. H. Runyon, in the factory of the Keystone Glass Co., Rochester, Pa.; machine-drawn window glass was first made in 1900 in the Arnold, Pa., plant of the American Window Glass Co., by the machine invented by J. J. Lubbers; and machine-drawn sheet glass was first produced successfully at Franklin, Pa., by the invention of I. W. Colburn (now the Libbey-Owens sheet-glass machine).

CHEMICAL RESEARCH LABORATORIES IN THE GLASS INDUSTRY

The Pittsburgh Plate Glass Co., whose products of manufacture include polished plate, window, optical, and black and white Carrara glass, and also refractories, has a research laboratory at Creighton, Pa.

The American Window Glass Company is not operating a research laboratory at the present time, although experimental work is in progress at Arnold, Pa., on pots and tank blocks.

The Hazel-Atlas Glass Co., of Wheeling, W. Va., manufacturer of glassware for packers' use, olive and vinegar bottles, ink containers, fruit jars, jelly glasses, hotel tumblers, amber ware, and blue and opal ointment jars, has research laboratories at Washington, Pa., and Clarksburg, W. Va., where research is centered on the improvement of the physical and chemical properties of glass and on the development of technical control. Raw materials are now purchased entirely by specifications, and control tests of operation are almost entirely under technical supervision. Among other accomplishments of this laboratory may be mentioned the production of some economical glasses and the improvement of the physical properties of glass for specific purposes. It is equipped with apparatus for the physicochemical study of glass and for the control of furnace operation.

The Macbeth-Evans Glass Company maintains a research laboratory at its Charleroi, Pa., factory. This company produces lighting, marine, railway, and laboratory glassware.

The H. C. Fry Glass Company and the Beaver Valley Glass Co., of Rochester, Pa., have derived many benefits from chemical research, but the outstanding accomplishment of their laboratory is the development of a translucent oven glass for baking purposes and other uses where heat-resisting glass is required. Other products of these related concerns are blanks for the cut-glass trade, cut glass, parabola and motion-picture lenses, plate and needle etchings, stemware, table tumblers, and cylinders for gasoline pumps. The laboratory has a glass furnace and small tank, and attention is being given at present to the application of glasses to the useful arts.

THE BRICK AND FIRE-CLAY PRODUCTS INDUSTRIES

Pittsburgh occupies a dominant position in the manufacture of face brick, refractories, and similar ceramic products. The monthly capacity of the plants in this section has been estimated to be approximately 20,000,000 nine-inch bricks; but at present the production is about 70 per cent of this figure, or a monthly tonnage of 49,000. The bulk of ordinary and special brick production in western Pennsylvania has an annual value of $15,648,000; this, taken together with other products manufactured from fire clay, gives a total ceramic products output of about $20,000,000 a year.

Research on Refractories

The Refractories Manufacturers' Association, an organization of 98 companies, has been conducting research in coöperation with the Mellon Institute of Industrial Research for a period of five years. The problems studied may be divided into three distinct classes, dealing with the manufacture, use, and testing of refractories. Among the manufacturing problems that of properly classifying the raw materials is perhaps the most important. It is necessary to study each deposit, either at the working faces or by means of drill cores, in order to obtain accurate information regarding the physical and chemical properties of the various sections. Slight variations in color, hardness or texture have been found to be indicative of a change in refractoriness, plasticity, or burning property. Investigations of this kind may result in the use of certain clays that have been rejected, in the rejection of clays that have been accepted, or in the separation of certain portions for special purposes.

After having determined the refractoriness of the various clays, it has been found essential to study their burning properties. Certain flint clays have little or no tendency to shrink, others have an inclination to vitrify, and plastic [illegible] to burn dense but attain their maximum density at different temperatures. When these tendencies are known, it is possible to devise mixes that have dense, open, or medium burning characteristics. Having these, the product will possess either high resistance to abrasion, high resistance to spalling, or properties that recommend it for general use.

Each step in the process of manufacture exerts a controlling influence upon the properties of the finished product. Even the amount of water used in developing plasticity affects the structure of the burned brick. Insufficient water gives an open product, as does an excess; an intermediate quantity gives a product of maximum density. Density is also influenced by the texture, molding pressure, and burn of the product.

Several problems pertaining to the use of refractories have been or are being studied. While it is often difficult to apply the results because of lack of information regarding the operation of most furnaces, this objection is disappearing rapidly with the development of recording devices.

A great many failures may be traced to furnace design, especially where brickwork is heated throughout, where the radiating surface is small as compared with the heating surface, or where the bricks are heated under pressure. Others may be traced to the mortar which has been used in laying up the brickwork. Certain mortars contain high percentages of basic fluxes. When fire clay is used, the brickmason often adds lime or portland cement to produce a cold set, little realizing the effect of these additions upon refractoriness. A reduction in refractoriness of 1000° F. is easily possible from this cause; as a result the mortar runs from the joints, leaves the brickwork exposed, and gives the appearance of high shrinkage.

Quite recently a relationship between furnace pressure and service has been established, based upon the fact that when a furnace is being operated under draft, cold air is drawn through the brickwork, helping to reduce its temperature. When the fuel is burned under pressure, the hot gases are forced through the brickwork, elevating its temperature, accelerating spalling, and causing premature failure. The disintegrating effect of several gases under various conditions is now being studied and the results to date indicate the possibility of their practical application.

Tests are being made constantly in the hope of associating the results obtained with service. Up to the present time the success of this study has been encouraging, but the work has been by no means completed.

Other Research in the Ceramic Industry

In the research laboratory of the Harbison-Walker Refractories Co., at Hays, Pa., several chemists are engaged in the development of refractories and the study of special problems pertaining to uses of refractories (fire clay, silica, bauxite, magnesite, and chrome). The special equipment of this laboratory embraces test kilns, load test, spalling-test and melting-point furnaces, and a Riehle crushing machine.

The Beaver Falls Art Tile Co., of Beaver Falls, Pa., manufacturer of glazed wall tile, maintains a laboratory where attention is given to the improvement of the product and the minimization of losses in plant operation.

THE WESTINGHOUSE LABORATORY

Year by year the annual value of electrical equipment manufactured in the district has increased, until in 1920 the total reached $165,000,000. Besides electrical utensils for the household, there are produced electrical machinery, dynamos, transformers, motors, and turbine engines; while in the new branch of radio-equipment manufacture a leading position is held, mainly because of the researchful attitude of the Westinghouse Electric and Manufacturing Company. This organization occupies more than 100 acres of floor space and employs 35,000 people.

The Research Department of the Westinghouse Electric and Manufacturing Company is located on Ardmore Boulevard, near East Pittsburgh, where problems under investigation pertain to the manufacture of electrical apparatus of all classes

Other Industrial Research Laboratories

Company	Products of Manufacture	Location of Research Laboratory	Important Accomplishments
Aluminum Company of America	Aluminium, including ingot, sheet, wire, foil, and other fabricated forms; bronze powder and collapsible tubes	New Kensington, Pa. (main laboratory)	Chemical research has been vital in the welfare of this organization, but no information is available respecting definite achievements of the present laboratory. The fundamental work of C. M. Hall has been described
Armstrong Cork Company	Cork products, cork compositions, linoleum and other floor coverings, and insulation	Pittsburgh, Beaver Falls, and Lancaster, Pa.	Perfection of high-temperature insulating brick and a material for cabinet-safe insulation; improved method for baking low-temperature, cork-board insulation; improved method of washing and bleaching cork stoppers; and new cork compositions
Duquesne Reduction Company	Copper and nonferrous alloys, made from secondary metals	Gross and Yew Sts., Pittsburgh	......
Electrolabs Company	Oxygen and hydrogen generating plants; acetylene apparatus	2635 Penn Ave., Pittsburgh	Levin cell; synthesis of precious stones in the corundum family; and methods for the detection of cotton in asbestos
Philadelphia Company	Manufactured (and natural) gas	Appliance laboratory, 553 Seventh Ave., Pittsburgh; gas manufacture laboratory, Elrama, Pa.	......
Rodman Chemical Company	Carburizing materials and special carbons	Verona, Pa.	"Patents issued as the result of work done in this laboratory dominate the manufacture of carburizing materials in this country"
Vulcan Detinning Company	Tetrachloride and bichloride of tin, tin crystals, fused caustic soda, and detinned steel scrap	Neville Island, Pa.	Development of "secret processes" in use by the company
Waverly Oil Works Company	Petroleum products	54th St. and A. V. R. R., Pittsburgh	Development of "thin-thick" oil or compound for internal-combustion engines

for power generation, distribution, and utilization. The department lists as its prominent achievements steel for magnetic work, effect of gases in metals, disk-pipe lightning arresters, radio tubes, electrical ceramic products, iron plating, standardization of bakelite, novel insulating materials, the study of heat transmission in insulators, sludging of transformer oils, and various new laboratory devices.

The Materials and Processes Department of the Westinghouse Electric and Manufacturing Company has a million-volt laboratory for power work and much special equipment for the investigation of chemical, physical, and electrical problems. Among its important accomplishments are radio apparatus, insulating materials, new alloys, high-tension phenomena, lightning arresters, and design data in many electrical lines.

The Department of Standards of the same company is also of interest, although strictly electrical in nature of work. It is concerned with standards, the standardization of meters, and the use of meters in all kinds of electrical measurements. There is considerable development work in progress, but all real research is done in the first-mentioned department.

The research laboratory of the Union Switch and Signal Company is engaged entirely in the study of physical and engineering problems.

RESEARCH IN OTHER PITTSBURGH INDUSTRIES

While the production of coal and coke, the manufacture of iron and steel, their products, electrical and railroad equipment, glass and glassware, and brick and fire-clay products, constitute the real strength of the high industrial position of the Pittsburgh district, there are many other branches of manufacture which have attained national prominence. Some of these industries have sprung directly from chemical research, while others of them have been and are being nurtured by it.

The Chamber of Commerce of Pittsburgh has reported that there are 300 lines of manufacture in and about Pittsburgh, most of them of a ferro-metallurgical character, but many being uniquely different. The production of radium has been mentioned. It may be noted here that the district leads the world in the production of finished aluminium, has the largest pickling and preserving plant in the world, and the greatest cork products manufacturing plant.

It has been estimated that the annual production value of the Pittsburgh industrial area is nearly $3,000,000,000 and that the yearly value of the products of the purely diversified industries amounts to $200,000,000.

Several other important industrial organizations having plants in the Pittsburgh district maintain research laboratories elsewhere. The American Zinc and Chemical Co., Langeloth, Pa., manufacturer of spelter, sulfuric acid, zinc oxide pigments, and zinc sulfate, has its investigational work carried out in the laboratory of the parent company, the American Metal Company, Ltd., in New York, N. Y. The Pittsburgh refinery of the Atlantic Refining Co., manufacturer of petroleum products, does no appreciable amount of research, laboratories for this purpose being operated at the Philadelphia plant. The Pennsylvania Salt Manufacturing Co., which has a works at Natrona, Pa., has its research laboratory at Greenwich Point, Philadelphia, where seven chemists are engaged in the study of processes for manufacturing heavy chemicals. Finally, the Gulf Refining Co., which has its general offices in Pittsburgh, maintains a large petroleum research laboratory at Port Arthur, Texas.

CONSULTING RESEARCH LABORATORIES

The R. H. Brownlee Laboratory, Inc., occupies the nineteenth floor of the Benedum-Trees Building, 223 Fourth Ave., Pittsburgh. This laboratory is specializing in petroleum refining, the design and installation of special refinery equipment, the preparation of utilizable products from natural gas, and rubber technology. It is equipped especially for investigational work in hydrocarbon and rubber chemistry. The R. H. Brownlee Laboratory has developed a new mixture of gases for use in metal-cutting and welding, a process for the production of gasoline, a new lubricating oil for airplane and automobile motors, and an improved process for making carbon black.

The Pittsburgh Testing Laboratory, 616 Grant St., is engaged in research on refractories, glass, and enamels, and on general chemical and metallurgical problems. The special equipment includes furnaces for the manufacture and testing of refractories, a metallographic outfit, apparatus [illegible], and complete facilities for work [illegible].

The Pittsburgh Testing Laboratory has perfected improvements in the manufacture of glass, dolomite refractories, and enamels for cast iron. The metallurgical researches of J. O. Handy have been technically important, his investigation of copper-bearing steel being particularly noteworthy.

THE PITTSBURGH EXPERIMENT STATION OF THE BUREAU OF MINES

The Pittsburgh Experiment Station of the Bureau of Mines, located at 4800 Forbes St., carries out, on an elaborate scale, research pertaining to safety and efficiency in the mining and metallurgical industries. Its laboratories are splendidly equipped with apparatus for the chemical and physical testing of explosives, furnaces for studying the combustion and inflammability of gases and dusts, and apparatus for research in hydrocarbon chemistry. There is a constant-temperature room, in which humidity, temperature, and air movement can be accurately controlled for making studies of the physical effects of these factors in connection with ventilation problems; and a gas chamber for investigations on gas masks and breathing apparatus.

The research accomplishments of this station are numerous. Among the outstanding achievements are the following: Solution of the problem of ventilating vehicular tunnels, such as the one under the Hudson River; determination of the effects of carbon monoxide in tunnels and mines and in the industries; effects of low concentrations and repeated exposures to carbon monoxide, etc.; development of new methods for determining the percentage of carbon monoxide in blood; determination of forms in which sulfur occurs in coal, coke, and gas, and reactions which it undergoes during carbonization, thus providing fundamental data for the desulfurization of coke; identification of the gum-forming constituents in manufactured gas, with a view to the elimination of gum deposits in meters and gas-distribution systems; determination of the solubility of trinitrotoluene, tetryl, and other explosives in various organic solvents; use of silica gel and other absorbents in removing sulfur and gum-forming constituents from coke-oven light oil; development of gas indicators for use in coal mines; and development of gas masks for industrial use.

CHEMICAL RESEARCH IN EDUCATIONAL INSTITUTIONS

THE UNIVERSITY OF PITTSBURGH

Chemistry in the University of Pittsburgh was placed on a high plane by the late Francis C. Phillips, distinguished generally for his investigations on natural gas, petroleum, and iron and steel, and the present staff of the Department of Chemistry has been able to enlarge the facilities for research and to elevate the standards in accordance with the best practice in chemical pedagogy. The departmental laboratories, while small, are well equipped for research in organic and physical chemistry and in glass.

The Departments of Chemistry and Chemical Engineering of the University have several advantageous coöperative arrangements with the Mellon Institute of Industrial Research, also a part of the University. The Mellon Institute [illegible] topics, thus affording direct contact between the students and specialists who are engaged in studying important problems of industry. The facilities offered by the Mellon Institute for systematic training in research methodology have led to the establishment of another coöperative relationship, which is even more valuable from a practical standpoint. Reference is had to the [illegible] in certain of the Industrial Fellowships of the Institute. According to this arrangement, properly qualified students in the Department of Chemical Engineering are placed in salaried assistantships during the periods when regular coöperative work is required. This plan carries the proviso that the student's thesis work is to be done under the direct supervision of the Industrial Fellow under whom the student has temporary employment. This system of temporary assistantships furnishes opportunities for the well-trained student to carry out technically important research and thus come to the notice of the manufacturer supporting the Fellowship on which he is employed. The outstanding importance of the arrangement, however, is that it gives opportunities for an intimate acquaintance with specific industries and their problems, as well as providing intensive training in scientific order in the application of research procedure.

Gas Chamber Used for Experimental Purposes, Pittsburgh Experiment Station, Bureau of Mines

Notable Investigations Conducted at Mellon Institute

Investigations	Industrial Fellows	Years
Physical properties of glass	E. W. Tillotson, Jr.	1911– ..
Bread technology	H. A. Kohman and others	1911– ..
Citrus products	F. A. McDermott	1912–1913
Electrical precipitation	W. W. Strong	1912–1913
Smoke investigation	R. C. Benner, John O'Connor, Jr., and others	1912–1914
Pressed glassware	S. R. Scholes	1912–1916
Chemistry of petroleum	R. F. Bacon, B. T. Brooks, W. F. Faragher, and others	1912– ..
Manufacture of carbon dioxide, carbon monoxide, hydrogen and nitrogen	R. H. Brownlee and R. H. Uhlinger	1913–1915
Composition flooring	R. R. Shively	1914–1916
Fractional distillation	M. A. Rosanoff and others	1914–1919
Hydrometallurgy of copper	R. F. Bacon, E. R. Weidlein, G. A. Bragg, and others	1914–1920
Olefin gases	G. O. Curme and others	1914– ..
Flotation of ores	H. P. Corliss, C. L. Perkins, and R. E. Sayre	1915–1921
Dental cements	C. C. Vogt	1915–1921
Chemistry of laundering	H. G. Elledge, A. F. Shupp, and others	1915– ..
Natural gas	J. B. Garner	1915– ..
Refractories	R. M. Howe and others	1916– ..
By-product coking	F. W. Sperr and others	1916– ..
Fiber container	J. D. Malcolmson	1917–1921
Heat insulation	G. D. Bagley and R. H. Heilman	1917– ..
Glue	R. H. Bogue	1917– ..
Insecticides	O. F. Hedenburg	1917– ..
Food and beverage flavors	M. DeGroote	1918– ..
Inks	F. F. Rupert	1918– ..
Protected metals	J. H. Young	1918– ..
Sulfur	H. S. Davis	1919–1921
Galvanizing	W. G. Imhoff	1920– ..

The present status of the Industrial Fellowship System of the Mellon Institute is presented in Director E. R. Weidlein's *Ninth Annual Report*, an abstract of which appeared in the preceding number of THIS JOURNAL. The Institute is a center for technical investigation in chemistry and allied subjects. Its purpose is to promote industrial success through scientific research; in other words, to find new materials and new processes for industrial development and to advance manufacturing through the application of scientific methods to industry. At the present time there are 51 Industrial Fellowships, or distinct lines of research, in operation, on which 88 chemists and engineers are engaged.

Of 200 technochemical inventions by Industrial Fellows of the Institute, the following are considered the outstanding ones from an economic viewpoint:

INVENTIONS	INVENTORS	DATES OF PATENTS
Synthetic resins ("redmanol")	L. V. Redman	1914
"Arkady" yeast food	H. A. Kohman, Charles Hoffman, T. M. Godfrey, and A. E. Blake	1915
Glass-making receptacle	S. R. Scholes	1916
Hydrometallurgy of copper	E. R. Weidlein	1916
Flotation of minerals	H. P. Corliss	1917
Shortening composition	H. A. Kohman, T. M. Godfrey, and L. H. Ashe	1917 and 1919
Flotation of minerals	C. L. Perkins	1917–1921
Absorbent material	J. B. Garner	1918
Manufacture of enameled ware	R. D. Cooke	1919
Synthetic acetylene	G. O. Curme	1919
Acetaldehyde, acetic acid, and acetone preparation	G. O. Curme	1919
Ethylene preparation	G. O. Curme	1919
Recovery of butane and propane	J. B. Garner	1919
Contact sulfuric acid process	H. H. Meyers	1919
Paint or varnish manufacture	F. W. Sperr and Marc Darrin	1919
Dental cement	C. C. Vogt	1919
Gasoline from natural gas	J. B. Garner	1920
Dry lime-sulfur product	O. F. Hedenburg	1920
Arsenate of lead	O. F. Hedenburg and D. S. Pratt	1920
Coating materials	J. H. Young	1920
Adhesive	J. D. Malcolmson	1921
Flotation of minerals	R. E. Sayre	1921
Liquid glue	D. K. Tressler	1921
Protected metal articles	J. H. Young	1921

THE CARNEGIE INSTITUTE OF TECHNOLOGY

The Carnegie Institute of Technology, located at Schenley Park, Pittsburgh, maintains a Division of Coöperative Research, the function of which is to encourage research throughout the institution and to establish research connections with industrial concerns. The Chemical Research Section has laboratories in each of three of the colleges of the Institute. Chief of these are the laboratories of chemistry and chemical engineering. These laboratories, located in the Science Building of the Engineering College, are at present occupied primarily with research on petroleum derivatives, and also the use of electrolytic methods in investigating certain nonaqueous solvents, colloids, and new alloys.

In the teaching laboratory of the Department of Industrial Chemistry, College of Industries, research is being conducted on the constitution of commercial products such as clay-jointing compounds, steel castings, and alloys. In the chemical laboratory of the Margaret Morrison Carnegie College for Women, analyses of soaps and of waters from many water systems are being made, and the effects of soaps and laundering processes on various fabrics determined.

The most important recent accomplishments in chemical research at Carnegie Institute of Technology are described in the article on "Some New Petroleum Products" by J. H. James, published in the February 1922 number of *Chemical and Metallurgical Engineering*.

The special equipment of the chemical laboratories of the College of Engineering includes: double-effect evaporator, Lummus extraction apparatus, Lummus diffusion apparatus, autoclaves, large hydrocarbon oxidizing apparatus, Cook compressor, motor generator, International oxygen-hydrogen cell, and fractional distillation outfit.

Related laboratories for research in pure and applied science are maintained by the departments of physics, metallurgy, mining, mechanical engineering, machine design, electrical engineering, and civil engineering. The problems studied are characteristic of Pittsburgh industries. The physics laboratories are engaged on problems of glass manufacture, such as the effects of varying compositions of borosilicates on the optical properties of glass. The metallurgical laboratories work largely on problems in iron and steel. Special equipment for metallurgical research includes apparatus for measuring fatigue-resisting properties of steels in drill pipe, drill rod, etc. The geology laboratory is studying Pennsylvanian shales and coals, and the faculty of the Department of Coal Mining has the coöperation of the staff of the Pittsburgh Experiment Station of the Bureau of Mines, in directing several researches on problems of engineering in bituminous coal mining. The Mechanical Engineering Department has concentrated chiefly on problems of lubrication, thermodynamics, governors, and steam-engine design. This department has detailed plans for an experimental rolling-mill, the erection of which is, however, awaiting the provision of additional funds. Such a mill is essential for the scientific study of roll-pass design and of the effects of varying pressures and speeds on the properties of the rolled steel.

Allied with these researches is the program of the departments of commercial engineering and industrial economics, which are at present engaged in a comprehensive study of the natural resources, power, transportation, labor and finances of the Pittsburgh district; while problems of marketing, sales-organization and industrial personnel administration are studied by the Bureau of Personnel Research. The cost of these researches is financed in large part by coöperating commercial and industrial concerns.

The Carnegie Institute of Technology aims to foster scientific research, because a research atmosphere is an aid to efficient instruction and because the institution recognizes its obligation to utilize to the full its facilities, both of brains and of equipment, in the service of the industrial community.

HOSPITAL RESEARCH LABORATORIES

Research in biochemistry is being carried out in several hospital laboratories, in addition to the Department of Physiological Chemistry of the School of Medicine of the University of Pittsburgh.

The William H. Singer Memorial Research Laboratory of Allegheny General Hospital, Sandusky Street and Park Way, N. S., Pittsburgh, is concerned principally with the study of medical problems, but several of the researches completed therein are of chemical interest. Reference is had to the work on the pathology of trinitrotoluene poisoning and on the bactericidal action of arsenical compounds on experimentally produced *Streptococcus septicaemia*.

The Magee Pathological Institute of Mercy Hospital is located on Stevenson St., Pittsburgh. Among its contributions to biochemical literature have been the following: Basal metabolic rate in constitutionally inferior children, rate of nitrogen elimination, a micromethod for blood sugar determination, and bacteriology of human cystic bile.

The new chemical laboratory of the St. Francis Hospital, 45th St., Pittsburgh, has begun research in biochemistry, although to date it has been engaged mainly in equipping the laboratory and standardizing technic for clinical use.

The laboratory of West Penn Hospital, 4800 Friendship Ave., Pittsburgh, is well equipped for pathological, bacteriological, and biochemical research. It has just completed an important investigation of the value of certain dried foods in the prevention of scurvy.

Pittsburgh as an Industrial Center[1]

By J. H. James and W. F. Rittman

Carnegie Institute of Technology, Pittsburgh, Pa.

IT WOULD be interesting if some writer in the field of industrial economics would trace the history of each of the industrial cities of our country, giving reasons, geographical and otherwise, that led to its specialization in manufacturing. These reasons in some cases have no connection with any strategic situation of the city in its transportation facilities, or its proximity to raw materials, but depend upon the accidental location in that place in its early days of a strong individual with the enthusiasm and the vision to work out the development of an industry that later dominated the district.

W. F. Rittman

Location and Transportation Facilities

Pittsburgh, the ninth city with its population of 600,000, is the hub of the fifth metropolitan district of the country, which immediate district has a population in excess of 1,200,000. Within the radius of a night's trainride there is a population of over 60,000,000, more than one-half the people of the country.

The geographical position of Pittsburgh alone is sufficient to have brought about the development of a great city. At the junction of the Monongahela and Allegheny Rivers, with the great Ohio stretching away to the southwestward, and being in water communication with all the valleys of the great Mississippi Basin, it holds a strategic position for distribution.

Pittsburgh is the central radiating point for six major railroads of the country, and thereby offers transportation facilities second to none. The tonnage originating in the Pittsburgh District is larger than the combined tonnage of New York and Boston, and is far in excess of that of any European port. The Monongahela River alone in 1920 floated 24,000,000 tons of freight, an amount equal to the combined tonnage of the Suez, Panama, and Kiel Canals.

Natural Resources

Remarkable as the factor of location has been in Pittsburgh's military and political history, this city would never have been anything but a distributing point for the great Middle West, had it not also had easy access to a most wonderful group of natural resources. These natural resources, coupled with the location and the indomitable spirit of the people, make her to-day "The Workshop of the World," and from the earliest days of the young republic we find here the utilization of these natural resources that are of prime importance to the industrial chemist.

For any manufacturing we must have, of course, first of all, a cheap and abundant fuel. Pittsburgh is in the heart of the northern half of the great Appalachian bituminous coal field. The "Pittsburgh Seam" is known the world over, and it is a satisfaction to Pittsburghers to know that at a lower level, and not yet mined to any great extent, we have the "Freeport Seam," insuring the supremacy of this district for years to come. The annual production from the Pittsburgh Seam alone is over 100,000,000 tons, approximately one-fifth of the country's bituminous coal output. The importance of this abundant fuel supply, with its resultant cheap power supply, is in itself a major influence and of primary importance to the industrial man, and more particularly to the chemical industry requiring power or fuel in a variety of forms.

The natural gas of the district is being sold at about one-fifth the cost of manufactured gas, when considered on a heat or B. t. u. basis. It is because of this natural gas supply that Pittsburgh is of primary importance as a glass manufacturing center.

Industrial Development

It appears pretty well settled that as early as 1795 there was established a window-glass factory of eight pots on the west side of the Monongahela River, and that General O'Hara erected his window-glass plant in the summer of 1797. At this time the population of Pittsburgh was 1565.

Glass manufacture gradually increased in volume. We find that the glass factories in 1804 turned out products to the value of $12,500, including window glass, bottles, jars, blue glass, and decanters. In 1807 the O'Hara works alone turned out $18,000 worth of products. In 1831 it is reported[2] that there were four window-glass houses and four flint-glass houses, employing 102 hands, using 7000 cords of wood, 150,000 bu. of coal, and turning out products to the extent of $500,000. Without spending time to trace the glass manufacturing development through the nineteenth century, it is sufficient to note that there was a steady and at times a phenomenal growth in this industry in Pittsburgh. For example, in 1886 we find that the use of natural gas had begun, and the operators were congratulating themselves on the more brilliant product obtained, particularly in the case of tableware and lamp chimneys.

J. H. James

While Pittsburgh cannot boast of such a scientific development of glass production as we have seen at Jena, yet there have been engineering improvements that represent equally as much in another direction—the writers refer to the machine production of glass bottles, etc., and the wonderful window-glass machine. Pittsburgh capital and Pittsburgh technologists have been closely connected with these developments, and from the modest beginning in the early part of the nineteenth century, to-day the industry musters 62 factories with over 3000 pots, an employment of 25,000 workers in normal times, and an annual payroll of over $20,000,000.

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[1] [illegible] presented at the 64th Meeting of the American [illegible] Pittsburgh, Pa., September 4 to 9, 1922.

[2] Thurston's "Pittsburgh's Progress," 1886.

Although glass manufacture preceded that of iron in Pittsburgh, it was not long before the iron ores of the district were smelted and a thriving business developed, particularly in making iron for castings. The rapidly growing country to the westward absorbed the products of these early furnaces and foundries.

It sounds strange in this day of beehive coke and by-product coke to hear that the first iron ores in this district were smelted with charcoal. George H. Thurston, writing in 1857, notes that the first "coke metal" was of inferior quality, but that later experience both at the blast furnace and the puddling furnace had obviated this difficulty.

In any discussion of Pittsburgh's iron and steel development it should be emphasized that the real inventor of the well-known Bessemer process was Kelly, a Pittsburgher.

Three important events took place in the latter half of the nineteenth century which placed the United States in the lead as a steel-producing country.

The first of these was the development of the Kelly-Bessemer process, and the second was the entrance of Mr. Andrew Carnegie into the steel business. Although Mr. Carnegie had already embarked in a small way in iron and steel manufacture, he at first opposed the adoption by his firm of the Bessemer process. The story goes that a little later he stood in an English steel plant watching a Bessemer converter in full blast. The spectacle of 30,000 lbs. of pig iron converted into steel in a few minutes changed Mr. Carnegie from a somewhat aimless investor and speculator into a steel enthusiast. It is still further related that this rapid and cheap production of steel opened up for him the vision of replacing all the wooden bridges of the Pennsylvania Railroad with steel structures, an accomplishment to which his firm later contributed largely.

The third great factor in the development of steel manufacture was the opening of the great Superior ore properties. The hard ore mines, opened in the seventies and eighties, and followed by the Mesaba in the early nineties, placed the United States ahead of any other steel-producing country in the world, and Pittsburgh, because of the fact that it was already an iron center, became the leading steel center of the United States and of the world.

The Bessemer ores, which served in the earlier part of the period outlined, have begun to decline, and we have had a gradual increase in the basic open-hearth process. Pittsburgh's natural gas has contributed in a remarkable manner to the cheap manufacture of steel from the Superior ores. With the present rapid decline in the natural gas supply, producer gas from bituminous coal is taking an important position in the steel industry.

The steel man is primarily interested in metallurgical coke, and as a result the by-product coke industry has been wedded to the steel industry. We have had a great deal of loose talk in this country about the belated development of by-product coke.

It should be pointed out that the steel industry is probably one of the most sensitive in the country to the fluctuations of business. The steel manufacturer would hesitate about the installation of an expensive by-product coke plant which he might have to close down within a year or so. Assuming a ready market at all times for all the by-products except the gas, he would be compelled to stock coke in a time of depression with no market for the gas. A market for gas means usually a contract with a local public utility corporation. Gas would be demanded for domestic purposes in dull times and in good times, but the steel man can use the gas in his own plants in good times.

All these objections, however, diminish when we see how by-product coke manufacture is handled by the United States Steel Corporation at its local Carnegie plants. At Clairton is now the largest by-product plant in the world, and work has already begun on an addition that will double its present capacity. The Clairton plant ran all through the recent business depression; this plant sends the gas to the steel mills at Duquesne, Edgar Thomson, and Homestead. By transferring business from other parts of the country to these plants, the Clairton by-product plant was kept in operation.

It seems certain, therefore, that as far as metallurgical coke is concerned, the by-product development will succeed best with the largest corporations.

It is but logical that along with the growth of "tonnage" steel manufacture we should have the manufacture of alloy steels. Crucible steel manufacture is an important factor in Pittsburgh's steel activities. At this point we should pay our tribute to the man whose vision and enthusiasm as a capitalist made possible the realization of the dreams of a chemist; the capitalist, the late Mr. Jos. M. Flannery, and the chemist, Mr. J. Kent Smith, worked over immense obstacles to the successful production of vanadium alloys. To-day, the company which they founded is the greatest producer of vanadium in the world, and a monument to these pioneers in a difficult field of metallurgical development.

The growth of iron manufacturing in Pittsburgh gradually attracted other industries which might be called iron subsidiaries: these include iron galvanizing, tin plate, sulfuric and hydrochloric acids, and in late years we have seen the interesting development of zinc and sulfuric acid manufacture here, as well as many other chemical industries (see table). The reasons, freight rates, markets, etc., which prompted capitalists to locate the latter industries in Pittsburgh, make an interesting study for the industrial chemist.

Although aluminium manufacture is now centered elsewhere, it should be remembered that Hall made his early experiments here, and that Pittsburgh capital supported him. The headquarters of the successor company is still in Pittsburgh, and one of the largest aluminium rolling mills is located near the site of Hall's early experiments.

Pittsburgh is becoming known as the "Electric City," because of its efficient means for changing coal into electricity. The district is served by two major utility companies, which are able to sell power on such favorable terms that most manufacturers, and particularly the smaller ones, prefer to purchase power in the form of electricity. The city has the largest steam power central station in America. The new Colfax plant has one operating unit of 80,000-h. p. capacity, with a second 80,000-h. p. unit now under construction. Ultimately, as the power demands increase, this one plant will have six turbines of 80,000-h. p. capacity, a total power development of 480,000-h. p. capacity. The combined electrical horse power of the two public utility companies serving in the Pittsburgh District will be about 1,000,000 h. p. The power generating plants are located directly adjacent and in direct open communication to the coal mines, making power as cheap, if not cheaper, than in any other locality in America.

The story of petroleum reads as much like a romance as the story of steel, and the discovery of petroleum and its ultimate utilization was the work of Pittsburghers. It seems will be remembered that Mr. George H. Bissell and Dr. F. B. Brewer of Pittsburgh were the prime movers in the formation of a company called the "Pennsylvania Rock Oil Company," which included some New Haven capitalists and Prof. B. Silliman, Jr., who was president. It was this company that employed Colonel Drake of New Haven to sink an artesian well. Work on this well was begun early in 1859 and oil was struck on August 28, 1859; the production was ten barrels a day without pumping and the oil sold for fifty cents per gallon.

The rapid growth of oil refining is shown by the following figures: in Pittsburgh, one year after the opening of the Drake well, seven refineries had been erected, bringing oil into use as an illuminator and a lubricator," as one of the local historians records it. In 1861, 17 new refineries were added; in 1862, 9 new ones, and in 1863, 15 additional were constructed. By the year 1867, the Pittsburgh district had 58 refineries and supplied over 60 per cent of the whole foreign exportation of petroleum.

While the later centralization of petroleum refining and the development of pipe-line transportation of the crude have changed the aspect of oil refining from what it was when Pittsburgh boasted of 58 refineries, this city is still a factor in the petroleum industry. The headquarters of many of the large oil firms are located here, and Pittsburgh's capital and technical skill are now going to all the oil countries of the world.

It may seem like an anomaly that, in a district dedicated to the element iron which has determined our engineering and material development, we should have the first large-scale development of the element radium, whose study has revolutionized chemical thought.

In 1911, Joseph M. Flannery of Pittsburgh with his associates organized the Standard Chemical Company, securing carnotite ore claims in southwestern Colorado and Utah, and having in mind the production from carnotite of radium and the associated values, uranium and vanadium. After large investments and discouragements that would have led an ordinary man to give up, the first production of radium on a commercial scale in America was made by this company in 1913. The chemical treatment of the ore is made at Canonsburgh, 21 miles southwest of Pittsburgh, and the final purification of the radium is made at the laboratory at Forbes Street and Meyran Ave., Pittsburgh. The production of radium was rapidly increased, owing to the demand for this material in Europe just prior to the outbreak of the war, the production in 1914 amounting to 9.6 g. of radium element. The company founded by Mr. Flannery is now the strongest concern engaged in refining carnotite ore, having produced 90 g. of radium since 1913, and possessing ore reserves capable of producing, on the lowest estimate, over 1000 g. of radium element in the finished product.

In speaking of Pittsburgh, one may refer to the corporate city, the county, or the metropolitan Pittsburgh District. The following table gives a list of Pittsburgh industries, with the number of plants located in each of these sections.

A study of the table shows that the metal and metal products industries hold first place. With 391 of these industries in Pittsburgh, 119 in Allegheny County outside of Pittsburgh, and a total of [illegible] in the Pittsburgh District, most of which are fabricating iron and steel and their products, it is apparent why Pittsburgh is called the Steel City and the Pittsburgh District is a steel center. These comprise 32 per cent of the [illegible] of the district.

As might be expected, the next largest industrial activity, [illegible] by the number of industries in the district, is that of mines and quarries, [illegible] coal, and numbering [illegible] in the district. The [illegible] industries ranking next are paper and printing, 297; textile and textile products, 193; clay, stone and glass products, 169; chemicals and allied products, 165; lumber and its re-manufacture, 96.

INDUSTRIES OF PITTSBURGH, ALLEGHENY COUNTY, AND THE PITTSBURGH DISTRICT

	Pittsburgh	[1]Alleg. County	Ptsb. Dist.
Aluminium and Its Products	2	3	8
Automobiles and Parts	35	41	46
Axles	3	4	5
Bars—Iron and Steel	13	22	32
Billets—Blooms and Slabs	8	12	19
Bolts—Nuts and Rivets	17	22	27
Brass and Bronze Products	23	32	39
Bricks	22	37	67
Canned and Preserved Goods	28	31	35
Cars and Parts	8	9	16
Castings—Iron and Steel	44	64	97
Cement	1	2	2
Chemicals	12	16	20
Cheroots and Stogies	23	23	27
Chocolate and Cocoa Products	1	1	1
Cigars	16	22	28
Clay	5	8	15
Coke—By-product and Beehive	10	12	52
Coal—Bituminous	142	207	479
Cork	3	3	4
Forgings—Iron and Steel	25	34	42
Gasoline	35	44	60
Glass Bottles	7	11	21
Glass—Lamp and Chimneys	0	6	9
Glass—Plate	4	8	10
Glass—Tableware	2	6	16
Glass—Window	2	2	6
Glue and Gelatin	0	1	1
Hoops, Bands and Iron Ties	7	11	14
Ingots—Iron and Steel	9	15	24
Iron—Pig	9	15	20
Lead	4	4	4
Machinery and Parts	47	55	72
Men's Clothing	32	32	33
Meters	2	3	4
Motors, Dynamos, Generators, Etc.	6	8	8
Oils—Crude	31	33	51
Oils and Greases	17	22	25
Oil Well Supplies	1	1	11
Paper—Printing and Wrapping	4	5	6
Pipes and Tubing	17	20	28
Planing Mill Products	39	57	90
Plates—Iron and Steel	4	7	9
Printing and Publishing	167	205	291
Pumps and Valves	8	8	13
Radium	1	1	1
Rails—Iron and Steel	1	2	2
Railroad Supplies	9	11	13
Refrigerators and Ice Boxes	3	3	5
Repair Shops	5	7	11
Sand and Gravel	14	17	25
Shafting—Cold Rolled, Drawn, and Turned	3	4	8
Shapes—Structural	13	16	19
Sheets—Iron and Steel	4	7	11
Ships and Boat Building	8	10	10
Slaughtering and Meat Packing	15	18	21
Sole Leather	1	1	1
Soap and Soap Powder	8	8	8
Springs	9	12	14
Supplies—Electrical	22	23	32
Stoves, Heaters and Ranges	14	14	21
Terra Cotta and Fire-Clay Products	11	14	38
Tin and Terne Plates	6	8	12
Toys and Games	3	4	6
Ware—Galvanized and Enameled	6	7	12
Washing Machines and Wringers	1	1	1
Wire Products	12	16	22
Woolen and Worsted Yarns	0	2	1
TOTAL	1064	1388	2180

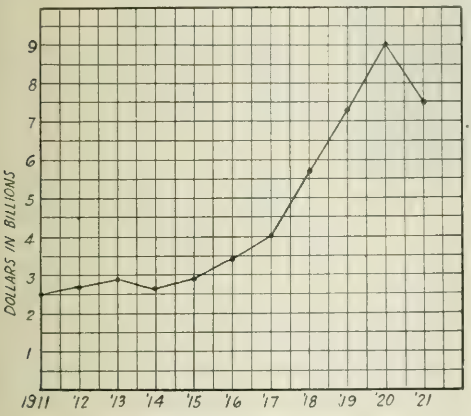
[1] Includes Pittsburgh.

FINANCIAL FACILITIES

Despite the generally accepted axiom that, given time, finance follows industry, the element of the credit and financial facilities of any community is important to the industrial leader, more particularly when the pioneer's facilities are such that he cannot wait on the "time" element. In making the financial appraisal of a community with a view of establishing an industry, the controlling elements are three: facilities for credit information, facilities for marketing commercial paper on a national scale, and availability of New

York finance. Through the evolution of various credit information bureaus, Pittsburgh to-day has facilities in this direction second to none in the country. Of the fifteen commercial paper houses in America to-day, four are located in Pittsburgh. This means, that should money be cheaper in San Francisco, or in any other community in America, than in Pittsburgh, by means of these commercial paper houses, the Pittsburgh manufacturer can get the benefits of that market.

In the element of finances, it is to be noted that the authors refer to availability to New York finances. This is a direct recognition of New York as the center of all major financing. Many cities attempt to show themselves as major elements in national financing projects, but a consideration of the transactions of their local stock markets and their achievements in financing large new industries as compared with New York, shows such claims to be without foundation. The effort of Pittsburgh financial leaders in dealing with national financial problems has not been one of financial competition with New York, but instead the effort and the result has been that Pittsburgh financial institutions to-day are able to offer their clients all the advantages of New York, Boston, and Philadelphia, as well as of Pittsburgh, either for the purposes of home manufacture or foreign trade.



Pittsburgh Bank Clearings, 1911–1921

Regardless of this, Pittsburgh as a financial community is in the forefront of American cities. With bank clearings in 1911 of about $2,500,000,000 these have grown to more than three times that much during the past decade. Pittsburgh has 78 banks and trust companies, with a capital of $63,000,000 and a surplus of $95,000,000, and with savings deposits of $323,000,000. One institution alone has a combined capital and surplus of $39,000,000, a figure which compares favorably with any financial institution in the world. The assessed valuation of Allegheny County's property is $1,800,000,000, an amount greater than any one of 34 states of the United States.

Such is a brief account of the industrial development of Pittsburgh. Enough has been given to show that the people who settled in this district have risen to the occasion in the development of their resources, and have met every challenge imposed by the city with reference to the developing valleys to the westward. To-day, Pittsburgh stands one of the industrial giants of the world, having satisfaction for work well done, and seeing even greater promise for future development.

The Paint Industry

By A. H. Sabin

Consulting Chemist, National Lead Co., New York, N. Y.

RELATIVELY little can be said of progress in the paint industry. During 1921 titanium oxide became important enough commercially to be recognized by the paint trade. It is produced by a single company; is obtained from a deposit of ilmenite (double oxide of titanium and iron) found in Florida associated with zircon, rutile, garnet, monazite, etc., from which it is separated by milling and concentrating; and then shipped to Niagara Falls, where it is treated in an electric furnace, and then leached with dilute sulfuric acid to make a crude titanium oxide. This is dissolved in strong sulfuric acid, and is then partly diluted with water. Barium sulfate (blanc fixe) is added, more water, and then treated until hydrated titanium oxide precipitates in intimate mixture with the barium sulfate. It is dewatered, calcined, and pulverized. The finished product contains 75 per cent of barium sulfate and 25 per cent of titanium oxide and is sold under the trade name of Titanox. As in the case of lithopone, the opacity of the final product is nearly as great as that of its opaque ingredient. Hydrofluoric is the only common acid which attacks it. It makes a soft film with oil, and is mixed with 25 to 40 per cent of zinc oxide to harden it.*

A. H. Sabin

The makers of lithopone claim that they are progressing in making it less liable to change by the action of light, and this seems to be generally conceded. It is said to be due not so much to any new discovery as to increased care and knowledge of the processes involved. Lithopone is used to some extent in outside paints, but two of the foremost makers express doubt as to its value for this use.

There appears to be nothing new in the paint vehicles. Perilla oil seems to have secured a permanent place, so much so that all offerings are taken, usually at a price above that of linseed oil; it is chiefly used in the varnish industry.

Research in Wood Finishing

Dr. A. H. Sabin, working in coöperation with the Forest Products Laboratory, the Engineering Foundation, and the National Research Council, is largely responsible for the organization of a committee which is going forward with the organization of research in wood finishing.

We have groups of men who are well versed in the characteristics of different woods and others who through research and experience have important data on finishing materials, but the two groups have not combined their knowledge on the solution of the problem of making articles of wood more enduring. There is much research still to be done, but the first work of the committee is the assembling of data in the literature, the reports of experienced painters and finishers, and in general the collection of what is known of the present state of the art. The initial work is being underwritten by industries concerned in the use of wood finishers and the work of research is being initiated at the Forest Products Laboratory, Madison, Wis.

Pittsburgh as a Center of Chemical Education

By E. H. McClelland

Technology Librarian Carnegie Library of Pittsburgh, Pittsburgh, Pa.

PITTSBURGH, by reason of its industrial supremacy, has long been characterized as "The Workshop of the World." The city has won wide fame also as a center of engineering activity. There is an old but unverifiable tradition that one in five of the engineers in this country spends some part of his life in Pittsburgh, and monuments to the ability of Pittsburgh engineers exist in the form of important engineering achievements in all parts of the world.

W. O. Breckon Studios

E. H. McClelland

Despite the recognition of Pittsburgh's preëminence in industrial and engineering lines, there has been little general realization of her importance as a center of chemical work and chemical training. This may be, in part, because the chemist's work, however important, is not spectacular and the results are not conspicuous, and because the layman does not understand the nature of chemical work and thus the public in general remains uninformed regarding the true significance of the chemist's achievements.

It has been said that 60 per cent of manufacturing is chemistry. This statement applies with particular force in the Pittsburgh region where the manufacture of the more important products, such as steel, glass, and coke, is under chemical control.

As a matter of fact, Pittsburgh is an important center of chemical industry, as will be competently set forth elsewhere in this issue of the JOURNAL. In the scientific control of this industry, as well as in chemical consultation and research, Pittsburgh employs thousands of chemists, and she is in very large measure training them to meet the demand.

From a recent survey of "Investment in Chemical Education in the United States, 1920–1921"[1] considering all the larger colleges and universities, it appears that Pennsylvania leads in the number of institutions reporting (33), is fourth in valuation of buildings and equipment ($1,854,852), and fifth in total investment in chemical education ($2,404,521). A considerable part of these totals, of course, represents institutions in the eastern part of the state, but there is a large number of colleges in western Pennsylvania, outside of Pittsburgh but within what is generally recognized as the "Pittsburgh District," and in Pittsburgh alone the total college enrollment is approximately 14,000.

ACADEMIC EDUCATION

UNIVERSITY OF PITTSBURGH—The University of Pittsburgh, formerly the Western University of Pennsylvania, first organized classes in engineering 80 years ago, and was the first institution west of the Allegheny mountains to grant engineering degrees. Of the older graduates, half of those now living are in executive positions, and approximately [illegible] industry.[2]

The teaching of chemistry was inaugurated at an early date, but the records are very scanty. A catalog of 1822 lists Rev. Robert Bruce as "Professor of Natural Philosophy, Chemistry, Mathematics, etc."[3] The first laboratory courses were introduced by John W. Langley (a brother of Samuel Pierpont Langley), professor of chemistry, mineralogy, and geology, in 1872–1873. Francis C. Phillips took charge of the work in chemistry in 1875. He says:

> In my early teaching the complete lack of equipment proved a serious obstacle. In answer to my earnest appeal for apparatus and chemicals the Chancellor was able to quote Sir Humphry Davy, who had publicly declared that a chemist needed only a few tobacco pipes and teacups in order to perform the most varied experiments. Assuredly this wicked and thoughtless remark of Davy's has done more to obstruct the progress of academic chemistry than did all his discoveries to advance it: because University presidents have made it a practice to know Davy's words by heart and have used them with appalling effect when the estimates for supplies were being pared down for next year's budget—a plain warning to us that we should in a spirit of kindness guard and protect our college presidents from reading the harmful literature of such undesirable citizens as Sir Humphry Davy.[4]

Dr. Phillips taught chemistry here for forty years. He won high renown as a teacher, while his research work brought him an international reputation, particularly in the field of gas chemistry. His work was so thorough that to-day gas chemists admit the accuracy of his results, and feel that they can with assurance begin investigation at the point where Dr. Phillips left off.

The University of Pittsburgh offers courses in chemistry and chemical engineering, and also trains men for M.S. and Ph.D. degrees. Dr. Alexander Silverman is head of the Department of Chemistry, and the faculty includes 5 professors, 6 instructors, and 14 assistants. Members of the professorial group hold the Ph.D. degree or have its equivalent in experience, while most of the remaining members of the faculty have the master's degree.

The Department of Chemistry offers 14 undergraduate and 22 graduate courses and certain special courses are offered by senior fellows in the Mellon Institute of Industrial Research. The courses for chemists and chemical engineers devote two years to each of the fundamental subjects—inorganic, organic, analytical, and physical chemistry—and include courses in sanitary chemistry, fuels, and industrial chemistry. One requirement of these courses is three years' work in modern languages. About 120 students were enrolled in chemistry and chemical engineering during the college year just ended.

In the work for advanced degrees, two-thirds of the work must be done in courses and one-third in research. The research may be conducted either at the University or in certain approved industrial laboratories in the vicinity. Forty-five graduate students were enrolled in these courses last year.

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[1] [illegible]

[2] [illegible]

[3] "The Western University in 1922," by Francis C. Phillips, **1919.**

[4] "The Old Western University at the Corner of Diamond and Ross Streets, Pittsburgh," **1914.**

The Department of Chemistry also provides training for undergraduates planning to enter engineering, medicine, and other fields, and the enrollment from these sources is 950. Some of the special engineering courses require considerable chemistry; for example, the course in oil and gas engineering—the pioneer course of its kind—goes pretty fully into organic chemistry and certain branches of chemical technology.

Carnegie Institute of Technology—Here courses in chemistry were taken by some 1800 students during the past college year. Sixty were registered in chemical engineering, in which an excellent course is offered under Dr. J. H. James, and a smaller number majoring in chemistry in the four-year course in science. (These figures do not include freshmen, as selection of courses is not made until the end of the first year.) Considerable attention is given to judicious guidance in the choice of these courses. In the former, encouragement is given to those whose qualifications are such that they are likely to be successful in the operating field, while the latter course is recommended to the more scholarly type of student who gives promise of developing into a research worker. The latter course naturally offers less of mechanics and engineering, and more of chemistry and physics, and in the senior year prescribes a brief research. Both courses include technical French and German.

The course on chemistry offered in the College of Industries is interesting and somewhat unusual. Instruction deals chiefly with the chemical properties of the materials employed in the three major departments of the College, namely, machinery production, building construction, and printing. The work of these departments stresses methods of economic production rather than creative design, the intent being to give such training as will enable the student to work into an executive position after a suitable period of employment in the industry. The chemistry taught is, in brief, the chemistry of materials in service. Prof. R. B. Leighou is in charge of this work, and his book, referred to elsewhere in this paper, is to some extent based on the course of instruction.

Following a foundation in general chemistry, organic, inorganic, and electrochemistry are introduced as the subject discussed may demand. Manufacturing processes are not emphasized; only such phases as have a notable effect on the properties of the products are studied in detail. For example, in discussing steels, attention is called to the fact that of two steels, one acid and the other basic open-hearth, the latter would be less suitable for castings, since it would probably be more oxidized because of the longer period in the furnace and the fact that it could not be deoxidized in the furnace on account of the phosphorus-bearing slag. In the accompanying laboratory work, for example, the permeability of paint films is determined; iron castings are examined for segregation of sulfides by making sulfur prints; and polished samples of steel are sealed up in air-free water to show that the steel will not corrode in the absence of free oxygen, thus indicating the effect on the metal in closed heating systems as compared with those in which the water is frequently changed.

In the Margaret Morrison Carnegie School for Women, chemistry is in charge of Prof. Charles Watkins. In addition to chemistry the young woman who is graduated from the Department of General Science has also had three years of training in biology, including bacteriology. Her training admits her to the best medical colleges and to the graduate schools of universities, and fits her for commercial work or for teaching. Many graduates now hold positions in hospital, industrial, and research laboratories.

The Carnegie Institute of Technology has just announced two fellowships in mining research, and two in teaching and research in coöperation with the Pittsburgh Experiment Station of the United States Bureau of Mines. The fellowships are open to graduates, and it is evident that chemistry will play an important part in the work, since the list of investigations announced includes such subjects as by-product coking and acid mine waters.[5]

Other Institutions—Pittsburgh has two other institutions of collegiate rank, Duquesne University and the Pennsylvania College for Women, and the curricula of both institutions include courses in chemistry.

The teaching of chemistry in Pittsburgh's secondary schools must not be overlooked. One of the recent high-school buildings, "Schenley High," cost the city nearly $1,500,000. It ranks among the first ten high schools in the United States, and its equipment for science teaching is vastly superior to that of many colleges and universities. Evidence of the thorough instruction in chemistry may be found in the character of the material in Pugh and Miller's "Problem Course in Chemistry"—a text which two of the instructors have prepared for their courses there.

Corporation Training

Concise but definite and systematic instruction in chemistry and metallurgy now forms a part of the required training of many salesmen and other nontechnical employees of the large steel companies. The pioneer development of these courses was the work of a Pittsburgh chemist, and the instruction now given here goes far to increase the competency of many employees who will never engage directly in chemistry or metallurgy.

Practical Training

Pittsburgh's contribution to chemical education is by no means confined to academic education. The industries of the Pittsburgh region maintain a very large number of chemical laboratories and each of these is a center of chemical training. The chief chemist of every industrial laboratory is a graduate teacher of the young college-trained chemist and, to an even greater extent, the instructor of the untrained practical chemist.

The staff of a large steel works laboratory may number 50 employees, many of whom enter with no training but with the well-defined purpose of becoming chemists. The training is intensive and the textbooks in many cases are the "Standard Methods" of the United States Steel Corporation. The number of entrants is very large and many of the ablest survive and pass on to positions of considerable responsibility. One who has been long acquainted with the steel laboratories can point to many men who, beginning as "carbon boys," are now assistant chemists, assistants preparing special solutions, etc.; and to a lesser number who have become able chief chemists or successful furnace superintendents. Though this practical work cannot be recommended as a substitute for theoretical training, it remains a highly important element in the education of chemists in industrial regions such as Pittsburgh.

Writing of Books

The creation of authoritative textbooks and reference books is an important factor in chemical education, and the service of good textbooks is by no means limited to their use in schools and colleges. Probably few Pittsburghers realize the extent to which the literature of science and technology has been enriched by the contributions of local authors. Several hundred such books and monographs are catalogued in the Carnegie Library of Pittsburgh and many of these are concerned with chemistry and allied subjects. A mere list of these would in itself afford worthy evidence of

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[5] *Science*, **55** (1922), 553.

Pittsburgh [illegible] chemical education.[6] Obviously complete enumeration cannot be undertaken here, but a few works may be mentioned as illustrative.

The widely read books of the late Robert Kennedy Duncan have been a source of instruction and inspiration to chemists and laymen, and by reason of their popular appeal have doubtless been instrumental in bringing many new disciples to the shrine of chemistry. "Chemical German," by the late Francis C. Phillips, has been adopted as a textbook in 28 educational institutions, and thousands of copies have been sold. "Technical Examination of Crude Petroleum," by W. A. H[illegible] and F. W. Padgett, has been adopted in seven institutions and has a large sale abroad. R. B. Leighou's "Chemistry of Materials of the Machine and Building Industries" is a valuable book, which in scope and treatment is not paralleled by any other American work. C. M. Johnson's "Rapid Methods for the Chemical Analysis of Special Steels" is the standard work in its field. H. P. Tiemann's "Iron and Steel" is without a rival as a concise encyclopedic dictionary of terminology and processes in ferrous metallurgy. S. L. Goodale's "Chronology of Iron and Steel" is unique in its field and constitutes a valuable reference work. "The Making, Shaping and Treating of Iron and Steel," by J. M. Camp and C. M. Francis, is the best existing work on American steel-mill practice. Privately published, and with no attempt at direct publicity, some 12,000 copies have been sold since the appearance of the first edition in 1919. Its high value in educational work is evinced by the fact that it has been adopted in more than 20 colleges, some of which have ordered well above 300 copies. The senior author, formerly chief chemist of one of the largest steel works in the Pittsburgh district, is also chairman of the Chemists' Committee of the United States Steel Corporation, and is thus in charge of editing the standard methods of analysis issued by the Corporation. These "Methods" have appeared in 8 pamphlets, some of which have reached a circulation of nearly 3000 copies.

Able specialists at the Pittsburgh Experiment Station of the United States Bureau of Mines are continually adding to their already valuable contribution to chemical literature, and among the forthcoming books by other Pittsburgh authors are important works on fuels, glue, glass, and metallurgical heating furnaces, on most of which subjects there are now few satisfactory books in the English language.

Lectures and Society Meetings

Public lectures constitute an important, if unsystematic, means of education. When delivered by men of culture and experience, they have a broadening influence, very efficacious in redeeming the prosaic life of the individual overburdened by routine. Pittsburgh is fortunate in having a wealth of this service concerned more or less directly with chemistry.

Most of the important national societies have regular section meetings in the city, and in addition there are several local organizations. The Engineers' Society of Western Pennsylvania, one of the strongest local engineering societies in the country, has many addresses on metallurgy and other subjects of interest to the industrial chemist. Fifty Pittsburgh women chemists, the largest group in any city of the United States who have completed regular courses in chemistry and are making it their life profession, have applied for an Iota Sigma Pi charter and expect as a feature of the coming [illegible] of the AMERICAN CHEMICAL SOCIETY [illegible] chemical society of women, of which [illegible] in the United States.

The United States Bureau of Mines contributes generously to education by means of its motion-picture films (concerned largely with chemical technology) and its mine-safety lectures and demonstrations (based in part on chemistry). These activities are nation-wide in service but both are entirely in charge of the Pittsburgh Experiment Station of the Bureau. The station is also responsible for numerous public lectures which in many cases are on chemical subjects.

The Mellon Institute of Industrial Research is a prominent feature in any survey of Pittsburgh's resources in the field of chemical education. The activities of the Institute will not be elaborated here, since elsewhere in this issue of the JOURNAL this subject will be ably presented. Aside from the systematic research work of the Institute, however, during the past season the public were admitted to some 30 technical lectures by staff specialists, and to a series of 12 lectures on "Scientific Method" by Dr. Walter Libby, one of the highest authorities on the history of science.

Library Resources

Chemical education, in the fullest sense, is broader than instruction in colleges and training in laboratories. In a very recent paper on "Aims and Means in College Education," Dr. Vladimir Karapetoff[7] says, "Every item of our knowledge is, or will be, contained in books and magazines," and indicates that the student's future success will depend very largely on his having learned how to use the resources available in literature.

Mr. Charles L. Reese, in discussing the work of the Research Information Service, in Washington, says:[8]

> If the scientific and technological literature of the world were regularly and systematically abstracted and listed, and if all this condensed information were available *** it is reasonable to anticipate that from 70 to 90 per cent of all requests could be answered directly and with reasonable satisfactoriness from this single master-key.

Any city, therefore, which is to acquire and retain high prestige as a center of chemical education and scholarly chemical work, must have adequate library facilities to enable its workers to get effectively in touch with the rich resources in the literature.

Pittsburgh is fortunate in having exceptional library advantages in the field of chemistry. The various research activities of the region (discussed elsewhere in this issue) in many cases include libraries. The Mellon Institute of Industrial Research, the Aluminum Company of America, the United States Bureau of Mines, the Pittsburgh Testing Laboratory, and other laboratories have well equipped library collections in their special fields.

The most important reference collection, however, is that of the Technology Department of the Carnegie Library of Pittsburgh, which was the first public library to establish a department devoted solely to scientific and technical literature. Something of what this library offers the chemist is set forth in an earlier paper[9] and only a brief review can be attempted here. Though this department is concerned with all branches of pure and applied science, it is especially strong in chemistry and metallurgy. Evidence of its strength in current chemical periodicals is shown by the fact that it contains approximately 80 per cent of the material abstracted in *Chemical Abstracts*. The greatest weakness is probably in medical and biological chemistry, but this gap is to some extent filled by the two local medical libraries (in the Pittsburgh Academy of Medicine and the Medical School of the University of Pittsburgh), and as the Technology Department of the Carnegie Library maintains a "union" card catalog of current scientific and technical periodicals in other local libraries, it is enabled to put patrons promptly in touch with this supplementary material.

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[6] A partial [illegible] by Pittsburgh authors appears [illegible] Library of Pittsburgh for July 19[illegible]

[7] *Engineering Education*, **12** (1922), 398.

[8] THIS JOURNAL, **14** (1922), 368.

[9] *Ibid.*, **11** (1919), 578.

In the selection of books the Carnegie Library of Pittsburgh probably makes more use of book reviews than does any other library, and in connection with this work the Technology Department publishes a quarterly "Technical Book Review Index," which is the only publication in the world devoted to recording reviews of new scientific and technical books.

The Carnegie Library of Pittsburgh is the only large library that regularly publishes a classified catalog in book form. The sections of this catalog dealing with scientific and technical books may be purchased separately, the latest series including books added to the collection during the years 1912–1916, inclusive. This catalog is brought up to date by a "Monthly Bulletin," which is annually provided with a subject index. These publications enable patrons at some distance from this library to keep much more closely in touch with the resources and growth of the book collection than is possible with most libraries.

The Technology Department has compiled and published many bibliographies on special technical topics. Among the subjects included are Lampblack; By-product Coking; Sewage Disposal; Mica; Sand; and Refuse and Garbage Disposal. A list of nearly 600 references on water-glass is now in press. The Technology Librarian compiles annual lists of new books on iron and steel and on the coal industry. These lists are published in local trade journals, and, through the courtesy of the editors, reprinted and distributed by the library. This department makes use of a "classified" card catalog—a type found in only two other large technical libraries, but which affords better service than the card catalogs generally found in libraries.

That the Technology Department is of some definite value to the chemists in the community is evidenced by the attitude of the local membership of the AMERICAN CHEMICAL SOCIETY. In 1921, a general reduction of municipal appropriations affected the library to some extent. Realizing that the funds available for technical literature were insufficient to maintain the service which this community deserves and rightfully expects, the Pittsburgh Section organized a Library Committee which, under the able leadership of Mr. J. O. Handy, raised among the local industries a fund of $2500 for supplementing the resources of the technology department, thus making possible the purchase of some important reference material. This fund was drawn upon also to finance an undertaking which enables this library to offer a special service not available elsewhere. A list has been made of the actual numbers identifying all patents in 48 complete classes of the U. S. Patent Office classification. These classes comprise approximately 200,000 patents, covering, in general, the entire field of chemistry and metallurgy. This is a field of great local importance and within its limits users of the library are now enabled to make a complete patent search by subjects—a service not possible with the printed indexes issued by the Patent Office.

So far as is known to the writer of this article, this work of the Pittsburgh Section is unprecedented in the history of any public library in America. Such action is a source of great gratification and encouragement to the library staff, and such constructive coöperation will go far to improve the library service in the community.

CONCLUSION

The character of the instruction in Pittsburgh's educational institutions, the close contact with her basic industries, and the superiority of her resources in chemical literature combine to make Pittsburgh an exceptionally favorable field for chemical education, while the nature and extent of her industries afford an important outlet for the product of this education. In confirmation of this statement, one interesting bit of evidence is found in the fact that many thoughtful technical students, after a year in contact with Pittsburgh conditions, change to courses in chemistry.

The Foundation for Chemical Development

By **W. A. Noyes**

UNIVERSITY OF ILLINOIS, URBANA, ILLINOIS

IN 1918, in the midst of the Great War, a society for chemical industry was organized in France. In one of the early numbers of the journal published by the society an estimate was given of the number of chemists in the leading countries before the war. According to this estimate there were 30,000 chemists in Germany, 5000 in England, 2500 in France, and about 16,000 in America. These numbers indicate very clearly that if America will use her opportunity she may soon hold the position of preëminent importance in chemistry held by Germany before the war. At such a time we should inquire on what foundation we must build if we are to seize the chance which surely lies within our grasp.

W. A. NOYES

Almost exactly one hundred years ago a young German of nineteen took his doctor's degree at Erlangen in Germany. After that he went to Paris to study with Gay-Lussac, for chemistry was at a very low ebb in Germany in those days and he chose to work with one of the greatest chemists of his time. There is such a thing as scientific heredity. It differs from physical heredity in that a man may choose his own father. And so Liebig chose Gay-Lussac, just as Wöhler, his intimate friend of later years, chose Berzelius, the Swedish chemist—the greatest chemist of that time. It is worth our while to remember, too, that it was only six years after the close of the Napoleonic wars, when France and Germany had been bitter enemies—but Liebig went to Paris to study chemistry. Two years later he returned home and at the age of twenty-one he was made assistant professor in Giessen, and in another year he was appointed full professor.

There in Giessen he founded a new school of chemistry. It was not so much a place where students were taught what was known of their science, as a workshop where students and teacher worked side by side in the endeavor to add something to the world's knowledge. To that laboratory men came from all over the world and from that laboratory went out influences that touch every chemist and, it might almost be said, every individual in the world to-day.

One of the students in Liebig's laboratory, A. W. Hoffman, was called to London in 1845 by Prince Albert, to fill a chair in the newly founded College of Chemistry. Ten years later he had an assistant by the name of William H. Perkin, only nineteen years of age. Young Perkin fitted up a small laboratory at home, and there he tried some experiments to convert aniline into quinine. We know now that there was not the slightest possibility of doing what he attempted. Instead he obtained a beautifully colored compound, the substance we call mauve. He tells us that at that time when chemists got a colored compound in their operations they were accustomed to throw it in the slop jar or remove it with boneblack. Perkin was struck with the beauty of the substance and he conceived the notion that it might be profitable to manufacture it for a dye.

The story of Perkin's difficulties and success is one of the romances of science and of industry. Benzene was not made by the ton then, as it is to-day. It was necessary to transform laboratory test-tube reactions into factory operations. Even when all these troubles were over and the mauve had been produced in quantity, the dyers who had been accustomed to Turkey red and fustic and indigo and other dyes of natural origin did not know how to use it, and Perkin had to go into their dyehouses and teach them.

Soon afterwards two German chemists, Graebe and Liebermann, demonstrated that anthracene is the mother substance of alizarin, the Turkey red obtained from madder root. They also succeeded in making alizarin from anthracene, but they did not succeed in establishing commercial production on the basis of their scientific discovery. Once more it was Perkin who did this in his factory, and within a few years the manufacture of alizarin from coal tar was so successful that the Dutch farmers had to give up raising madder root. Even as early as 1880 it was estimated that the alizarin which was manufactured from anthracene at a cost of $8,000,000 a year would have cost $28,000,000 if it had been prepared from madder root. It is scarcely an exaggeration to say that enough has been saved from this to pay for all the university laboratories in the world.

With such a beginning one would think that the coal-tar dye industry belonged to England. The initial great success was achieved there, and the coal tar from which the dyes were made was produced in much larger quantities in England than on the continent. But within a few years the new industry was almost completely transferred to Germany. At the beginning of the Great War the value of the product of this manufacture was estimated at about $100,000,000 annually, from two-thirds to three-fourths of the whole amount being made in Germany. We used in America dyes to the value of about $17,000,000, but manufactured only about $3,000,000 worth ourselves. Why should Germany so far surpass all other countries in this industry? The chief reason undoubtedly was that Germany had a larger number of chemists trained in methods of research in the spirit of Liebig's laboratory. There were other reasons that we do not like so well. Over and again American manufacturers tried to make aniline and other substances called "intermediates" which are used for the preparation of various dyes. In every case German manufacturers took care that the price of the article made was put so low that the American manufacturer was forced out of the business.

A few years ago our sailors were in danger of going to meet the submarines, blind, because we could not manufacture the optical glass needed to make the necessary instruments. In such an emergency to whom did we turn for help? To the manufacturers of glass? No, we appealed instead to men trained by many years of research at the Bureau of Standards and at the Geophysical Laboratory in Washington, where they had been studying silicates, not for the purpose of making glass, but in order to discover how the rocks have been formed. These men were able to attack the problem, and with the aid of a manufacturer they were ready to furnish six different kinds of glass within a few months. Then a seventh different glass was called for. Meanwhile, they had worked out the so-called triaxial diagram for silica, potash, and litharge, by means of which they could predict the relation between the composition of a glass made from these ingredients and its index of refraction and dispersion. They located on this diagram the composition of the glass having the desired properties, put the materials together, and it came out right the first time. Such is the difference between the old cut and dry methods of so-called practical men and a genuine scientific method.

Universities are not the only institutions where researches are prosecuted. It was at the Royal Institution of London that Sir Humphry Davy made those brilliant discoveries in electrochemistry which lie at the foundation of the great electrochemical industries of our time. There Faraday discovered the laws of electrical induction, that an electrical current could produce mechanical motion, and that mechanical motion could produce an electrical current. Those were principles which carried the germ of every machine used to generate electricity and of every electrical motor in use to-day.

Not long ago the Dean of a College of Commerce in one of our state universities made the statement that there are two ideals in vogue in these schools. One is that the students shall be trained primarily to do some specific thing—to be a stenographer, a bookkeeper, an accountant or something of that sort—in short, that the training shall be vocational. The other idea is educational, the laying of a broad, thorough foundation for future work. He spoke emphatically in favor of the second ideal. Thirty years ago many of us got the impression that the steel industry was calling for chemists who could make steel analyses just as those analyses were made in a works laboratory. That was training for a trade, not for a profession, and many young men trained in that way found that they were soon displaced by high school lads or boys of even less training, who could carry out the mechanical manipulations required as well as they. It was only those with a broader, professional training who continued successfully in work as chemists. We often tell our students that it is fully as important to secure good training in mathematics, physics, German, and French as it is to study chemistry while in college. If they are successful as chemists they will continue to study chemistry all their lives but they will probably never again find such a good opportunity to study the other things essential as a foundation for their work.

A thorough knowledge of chemistry and of related sciences is not enough. It was not knowledge of chemistry, merely, nor, indeed, chiefly, which made the men trained in Liebig's laboratory so efficient. It was not knowledge alone which made many of our chemists and physicists so efficient in the emergencies of war. The factor of far greater importance was the habit of research, the ability to attack new and strange problems and solve them quickly. Chemical knowledge was much more limited one hundred years ago than it is to-day and the young men in Liebig's laboratory were given the joy of research work after comparatively brief preliminary training. It now takes several years to gain that elementary knowledge of inorganic, analytical, organic, and physical chemistry which we think essential. Our students certainly do not get a too comprehensive knowledge of these subjects but it is a question whether we do not carry the process of cramming too far before we give them an opportunity to begin constructive work. As teachers, too, there may be a question whether we are not sometimes more anxious that they should get results of interest to us rather than that they should acquire the habit of solving difficulties for themselves with a minimum of guidance from others.

Progress in the Chemistry of Naval Stores, 1920-1921[1]

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DURING the past two years there have been numerous contributions to our knowledge of the chemistry of naval stores, of which oil or spirits of turpentine and rosin are the most important. Probably because of its more widespread and divers uses, and also because of the fact that its composition and constitution are less well understood than is the case with turpentine, more work has been done on rosin than on turpentine. Even now the constitution and exact composition of rosin are not definitely settled. We shall consider the subject at hand under three major headings: first, the crude resin or gum; second, turpentine oil or its constituents and closely related compounds; and third, rosin and its products.

F. P. Veitch

Resin and Gum

Among the less well-known sources of turpentine and rosin are the pine forests of China. There is quite an appreciable quantity of rosin exported from China, principally to Japan and Australia. Shinosaki and Ono[1,*] obtained the following results from a sample of crude Chinese resin: essential oil, 8.5 per cent; rosin, 84.35 per cent; loss, impurity, and water, 7.5 per cent. The essential oil consisted largely of *l*-α-pinene, with a trace of dipentene and about 11 per cent of a new tricyclic sesquiterpene. Heurich[2] has examined the oleoresin from the Norway pine, *P. sylvestris*, the source of turpentine in Germany, Poland, and Russia. The yield of essential oil and rosin, as well as their composition and properties, is stated to correspond to those of American turpentine and rosin, except that the oil is levorotatory, in this respect simulating French turpentine. A possible new source of naval stores in India is the tree known as *Boswellia serrata*, or Salai tree. The resinous exudation, known locally as salaigugul, is a gum-resin containing, beside essential oil and rosin, about 20 per cent of soluble gum. Fowler and Malandkar[3] have worked out a method of separating the rosin and the gum, after removal of the oil by steam distillation, in which the resin is hydrated by heating with water under pressure. The hydrated resin floats on the surface and can be removed as a solid on cooling. The gum forms a flocculent precipitate on the bottom of the vessel. It has weak adhesive power. The hydrated resin is subsequently dehydrated by heating. It differs from ordinary pine rosin principally in acid and saponification numbers, which are, respectively, 51.6 and 61.3. These low values make the rosin useless for soap making, but it may be useful for varnish making.

In a series of articles, G. Dupont[4,5,6] describes the results of his investigations on the resin of the French maritime pine. The two isomeric acid constituents, *d*- and *l*-pimaric acids, show marked difference in the stability of their rotatory power. The rotation of *d*-pimaric acid was not changed by the action of very dilute HCl, but *l*-pimaric acid showed decreasing rotatory power according to the length of time in contact with the hydrochloric acid, up to 24 hrs., after which the rotation increased again slightly. He considers the abietic acid in rosin as a mixture of isomorphous acids which he designates as pimarabietic acid, produced by the action of heat on the pimaric acids of the crude resin.

V. E. Grotlisch

Turpentine

The terpenes, of which pinene, the principal constituent of turpentine, is probably the best known, constitute a large and complex class of compounds. Only those bearing a direct relation to turpentine and its constituents are considered in this review. Simonsen[7] has found a new bicyclic terpene, *d*-carene, and a new tricyclic sesquiterpene, which he calls longifolene, in the Indian turpentine oil obtained from the Chir pine, *P. longifolia.* The author ascribes to these two new compounds the two properties of Indian turpentine which make it inferior to the American or French product, namely, ease of oxidation and high per cent of residue on evaporation. Although not oxidized by a mixture of dichromate and sulfuric acid, *d*-carene readily absorbs oxygen from the air, as shown by the fact that one cc. of this compound, when placed in a closed vessel (dimension not stated), absorbed all the oxygen from the air in three days. Analytical constants for the new compounds are given.

The preparation of synthetic rubber and synthetic camphor has occupied the attention of chemists, more particularly in Europe, for many years. If economically successful, it would open up a wide field for the use of turpentine. In order to throw some light on the conditions governing the formation of isoprene, as well as to check up a theory advanced some years ago that limonene or dipentene gives better yields of isoprene than pinene, Mahood[8] passed the vapors of turpentine, both from gum spirits and steam-distilled wood turpentine, through heated tubes, with and without catalysts, under carefully regulated thermal conditions. His results indicated that limonene, or rather the turpentine fractions consisting largely of limonene, did not give any marked increase in the yield of isoprene, and that gum turpentine was just as good as wood turpentine. The small yields of both isoprene and toluene preclude any economic disposal of turpentine [illegible]. The production of synthetic camphor, however, [illegible] considerably more promise, from an economic point of view, than the manufacture of synthetic rubber from turpentine. Luttringer and Dubosc,[9-16] in a series of articles, have described a number of methods of treating turpentine or derivatives thereof, principally pinene hydrochloride, to obtain esters which can be easily converted into camphor. Along this same line, Wesson[17] has patented a process of converting pinene hydrochloride into isobornyl esters, based on the action of certain organic acids in the presence of zinc as a catalyst. An interesting review of the patent literature on the manufacture of synthetic camphor has been published by Witte,[18] the author going back to some of the earliest patents taken out in Germany. The practicability of some of the patents, in the light of our present knowledge on the subject, is also discussed. The Fabrique de Prod. Chim. de Thann et Mulhouse[19] has patented in England a process for obtaining optically active borneol, free from isoborneol, based on the reaction of pinene and tetrachlorophthalic acid.

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[1] Published by permission of the Department of Agriculture.

[*] Numbers in the text refer to Bibliography at end of paper.

Pariselle[20] has separated α- and β-pinene from a large volume of French turpentine by very careful fractionation *in vacuo*, and checked up their physical constants. By the action of hydrogen bromide both compounds gave the same two hydrobromides, one solid and the other liquid. Bromine in carbon tetrachloride solution, at low temperature, gave a complex mixture of addition and substitution products, containing both bromides and hydrobromides. A monobromide and two dibromides were isolated.

Henderson and Marsh[21] obtained three pinene dichlorohydrins, soluble in water, by the action of a dilute aqueous solution of hypochlorous acid on pinene. In one of the papers of their extended series on the chemistry of pinene, Ruzicka and Trebler[22] dispute the constitutional formula for nitrosopinene advanced by Wallach, and advance one based on their own observations.

ANALYSIS

The analysis of turpentine is largely confined to detection and estimation of adulterants and for compliance with specifications. Hofman[23] has described a simple method of detecting adulteration of certain essential oils, among them being turpentine. These oils are relatively insoluble in alcohol at ordinary temperatures. The oil is dissolved in four volumes of alcohol by warming, the concentration of the alcohol depending upon the oil under observation. Ninety per cent alcohol is used for turpentine. If the turpentine is pure, the solution should start to become turbid, indicating separation, at about 60° C. Allina and Salvaterra[24] and Salvaterra[25] have described methods of determining mineral oil in turpentine, for which they claim greater accuracy than is shown by most of the practical methods now in use. Their methods are based on the formation of nonvolatile compounds by the absorption of bromine or iodine by the terpenes to the point of complete saturation. The volatile unchanged mineral oil is then removed by steam distillation. The application of the methods (especially Salvaterra's iodine method) is rather expensive, however, on account of the high cost of the reagents used, since turpentine absorbs over three times its weight of iodine, and considerable excess must be used to insure complete reaction.

Very few methods have been published on the determination of coal-tar oils, such as toluene, xylene, and solvent naphthas, in turpentine, probably on account of the relative infrequency of such adulteration. Grotlisch and Smith[26] have worked out a method which is not only applicable to adulteration with small percentages of coal-tar oil, but also detects the presence of mineral oil. Some of the pinene of the turpentine is removed by conversion into the solid pinene hydrochloride, and the adulterant concentrated by fractional distillation of the filtrate at reduced pressure. The distillate containing the adulterant is then sulfonated to destroy the remaining terpenes and to form sulfonic acids of the coal-tar hydrocarbons. Steam distillation of the sulfonation mixture separates any unchanged mineral oil that might be present. Finally, the sulfonic acids of the coal-tar hydrocarbons are broken up with recovery of the oils themselves, by direct heat distillation.

Specifications for turpentine have heretofore been far from uniform. Based on the results of examining a considerable number of commercial pure turpentines, the U. S. Interdepartmental Committee on Paint Specification Standardization[27] has adopted and published a set of "Recommended Specifications for Turpentine," which have been adopted by various bureaus of the Government and other agencies as standard specifications for turpentine. Instructions for sampling, analysis, preparation of reagents, and a basis of purchase, which take account of the expansion and contraction of turpentine with changes in temperature, are given. A handbook on turpentine has been published by Veitch and Grotlisch[28] containing, besides the above specifications, a review of the principal sources of turpentine throughout the world, the principal uses, process of manufacture, methods of transportation, expansion tables, simple methods of detecting adulteration, review of state laws covering the sale of turpentine, statistics on production and exports, and a method of calculating capacity and outage of tanks.

USES OF TURPENTINE

By far the largest proportion of turpentine is used as a thinner in paint and varnish. Several interesting new uses have recently been described. An anonymous article[29] describes the use of turpentine in a bleaching liquor said not to affect the strength of the fiber of the cloth, as chlorine often does. Several formulas for preparing the "ozonized" turpentine are given. Another interesting new use is described in a patent by Pratt.[30] A sulfur-terpene compound known as "toron," in the form of a black viscous liquid or semisolid, is prepared by heating turpentine with sulfur. It is used for waterproofing canvas, preparing rubberized cloth, and as a bond for attaching or coating metal surfaces with genuine rubber. The physiological effects of turpentine vapors when turpentine is used in quantity as an extraction medium for fats, waxes, etc., are discussed by Lewin.[31] Turpentine is classed as a narcotic type, producing depression of the nervous system, and may cause eruption of the skin and mucous membrane.

ROSIN

One of the less well-known constituents of rosin is a body called retene. Virtanen[32] has attempted to throw some light on the relationship between retene and the resin acids by preparing hydrogenated retenes and studying their chemical properties. One peculiarity brought out is the stability of the hydrogenated retenes toward permanganate, although they are unsaturated bodies. Aschan and his co-workers[33,34,35] have described and investigated a new resin acid, called pinabietic acid, which they obtained from a Swedish pine oil. Its molecular weight indicates the formula $C_{20}H_{30}O_2$, thus being isomeric with abietic acid. It does not, however, show the same color reaction by the Mach† test as abietic acid. A striking peculiarity is the difference in rotation in various solvents. It is dextrorotatory in the aromatic

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Monatsh., **15** (1894), 627.

hydrocarbons, and levorotatory in alcohols, ether, and chloroform. By adding absolute alcohol to the solution in benzene, the rotation can be changed from positive to negative, with a zero reading in a mixture of 92 per cent of benzene and 8 per cent of alcohol. It is nearly insoluble in petroleum ether and ligroin. A constitutional formula is given.

Aschan[36] claims to have discovered and describes a new series of acid bodies in rosin which he calls colophenic acids, with a general formula $C_nH_{2n-10}O_4$. Several methods of separating them from rosin are described. The author believes that it is owing to the presence or formation of these acids that the dark color of low-grade rosins, as well as the bitter taste, is due. The dark color of the "leim-galle," the precipitate which forms on boiling a solution of rosin size, is also supposed to be due to these bodies. They are amorphous, highly unsaturated, and instantly decolorize permanganate. Fahrion[37] has taken issue with Aschan as to the originality of the discovery of these bodies in rosin. He claims that they are identical with the so-called oxyabietic acids described by him in a previous work†† on the atmospheric autoxidation of powdered rosin. In a later article Aschan[38] refutes Fahrion's claim to priority, and shows that there is no relation between Fahrion's oxyabietic acid and the colophenic acids.

Grün,[39] on the basis of his observations, has attempted to formulate a structural formula for abietic acid to show its relation to α- and β-pinene. He discusses the possibility of the formation of abietic acid by the union of one molecule each of α- and β-pinene. Stock[40] has distilled rosin under the high vacuum of the green cathode ray, *i. e.*, practically a complete vacuum. It was possible to distil it almost completely without appreciable decomposition. The relatively small difference in temperature between the boiling liquid rosin and the vapors proves that rosin does not contain polymerized bodies of abnormally high molecular weight. He obtained crystalline acids from amorphous rosin by heating *in vacuo*, the time required to effect complete change depending on the temperature used. Among his conclusions is the following on the composition of rosin: α-abietic acid, 31 per cent; β-abietic acid, 31 per cent; γ-abietic acid, 19 per cent; resenes (or retenes) 10 per cent; essential oil and bitter principles, 0.5 per cent; impurities, 0.5 per cent.

ANALYSIS

The detection and determination of rosin in mixtures and preparations is probably the most important phase of rosin analysis, since it is seldom bought on specification and not much subject to adulteration. Wolff[41] has described a method of detecting and approximately estimating the rosin in oil varnishes. He finds it necessary to isolate the resin acids, since boiled linseed oil, especially in the presence of manganese driers, sometimes gives a reaction with the Storch-Morawski test which closely approaches that of rosin. Neither rosin which has been heated to high temperature for some time nor rosin esters give a characteristic color test. McNicoll[42] has published a method for determining resin acids in fatty mixtures, depending on the esterification of the fatty acids by naphthalene-β-sulfonic acid, leaving the resin acids unchanged. These are titrated or separated and determined gravimetrically. More reliable results are claimed than by former methods, such as Twitchell's.

USE OF ROSIN

The three principal uses of rosin in order of their importance in the United States are the manufacture of soap, paper size, and varnish, soap makers using about as much as the other two industries together. A bibliography on the use of rosin in soap-making has been published by Jungkunz,[43] which also includes a discussion of the methods of determining rosin in soap. German rosins, prepared in Germany from the resin of *P. sylvestris*, seem not to have measured up to the imported American and French products, especially from the soap-makers' standpoint. Goldschmidt and Weiss[44] have examined several samples of German pine resin, from which they prepared the rosin by the use of solvents. Their analysis of these brings them to the conclusion that German rosin is not greatly inferior to American or French rosin, so far as acid and saponification values and per cent of unsaponifiable are concerned. Goldschmidt[45] found that rosin, when left in lump form, showed up better on the "stearin" method* for available rosin substance, *i. e.*, the soap-making power or value of the rosin, than powdered rosin. They conclude, from the results obtained on powdered rosin which was exposed to moist air for some time, that a water-soluble oxidation product is obtained, which is lost during the analysis by escaping solution with other resin acids in the ether.

The application of rosin to the sizing of paper has brought out a number of new ideas. Thindon[46] concludes from recently published data that the sizing property of rosin is due to free rosin which in turn is protected by a film of aluminium hydroxide or resinate. Traquair[47] states that by dissolving the size and alum in a suitable starch solution the quantity of rosin required can be reduced by about 50 per cent. Sutermeister[48] seems to think that high-grade rosins gave better sizing efficiency than low grade, but the difference between them hardly warrants the payment of any material difference in price.

Sieber[49] has investigated the behavior of a suspension of free rosin toward various electrolytes. The suspension was precipitated by $Al_2(SO_4)_3$ at a concentration of 0.00261 mols. per liter. Calcium and magnesium salts required 0.025 and 0.015 mols. per liter, respectively, to precipitate the rosin. From this he concludes that hard water does not materially affect the suspension of free rosin. Schneider[50] also discusses the bad effect of hard water on size emulsions containing a high percentage of free rosin, and further points out that a size emulsion should not get above 100° F., since aluminium resinate starts to solidify or coagulate at this temperature, losing its finely divided form. Miles[51] has taken out a patent for oxidizing rosin by agitation with H_2O_2 until it is capable of forming an ammonium compound which may be diluted indefinitely with water, thus being adapted to paper sizing.

Within the past five or six years the use of rosin in varnish-making has increased markedly, owing to the discovery that rosin could be esterified, reducing its acid value and increasing its hardness and weather resistance. Very satisfactory varnishes are now made from rosin esters and tung oil. Gardner and Coleman[52] have described a process for the esterification of rosin with glycerol and tung oil in the open varnish kettle, using hydrated lime or calcium soaps as catalysts. Formulas for several different classes of varnish are given.

Sterling, Grotlisch, and Veitch[53] have patented a process of esterifying rosin with glycerol using zinc as a catalyst, whereby very low acid values are obtained. Murray[54] has investigated the various conditions governing the esterification of rosin with glycerol. A very satisfactory product is obtained by esterifying with somewhat less than the required quantity of glycerol for complete neutralization, and completing the latter with lime. An interesting point brought out is the fact that a good rosin ester approaching kauri can be obtained by esterifying a mixture of one part rosin and three parts congo copal, but the process must be carried out in an aluminium vessel instead of copper, since the latter acts in a catalytic manner, setting the mixture of resins before esterification can take place.

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†† *Z. angew. Chem.*, **20** (1907), 356.

* Goldschmidt and Weiss, *Seifenfabr.*, **39** (1919), 49; C. A., **13** (1919), 1942.

Jahn[55] has examined the properties of mixtures of rosin and beeswax, and found that under certain conditions solid solutions are formed, or mixtures in which the solid solution of rosin in wax is in equilibrium with pure wax. Changes taking place on storage of such mixtures are described. Gerstacker[56] has examined what he terms a "distilled rosin," the residue or product obtained by only partially breaking down rosin and volatilizing the oil formed. He gives the properties of the bodies obtained by heating the rosin at 310° to 320° C. and at 350° to 370° C. Strange to say, the latter product is the harder of the two. Neither is entirely soluble in a mixture of alcohol and chloroform.

MISCELLANEOUS

Hübscher[57] describes a product obtained in Sweden as a by-product in the manufacture of chemical wood pulp, which is known as "tall-öl," or Swedish rosin oil or pine oil. The crude product is refined by distillation leaving a so-called "tall-öl pitch." Recipes for using the products are given.

Shippen and Griffen[58] have investigated the properties of emulsions made from pine oil and other oils obtained by the distillation of pine wood, with reference to their value as antiseptics and bactericides, along the line first pointed out by Stevenson.** They substantiate some of the earlier findings of Stevenson, notably that steam-distilled pine oil gives a more active disinfectant than the destructively distilled oils. They conclude, however, that disinfectants of this type have only a limited value, since they failed to kill *Micrococcus aureus* and *B. anthracis* in any dilution capable of emulsification. For killing *B. typhosus* in a limited time, a dilution of $^1/_{100}$, or 1 per cent, is recommended even though a $^1/_{800}$ dilution killed when in contact with the organism for a longer time.

BIBLIOGRAPHY

1—Y. Shinosaki and T. Ono, "Chinese Pine Resin and Gum." *J. Chem Ind. (Japan)*, **23** (1920), 45; *C. A.*, **14** (1920), 2928.

2—H Heurich, "On the Constituents of the Gum of *Pinus sylvestris*." *Z. angew. Chem.*, **134** (1921), 363

3—G. J Fowler and M. A. Malandkar, "Extraction of Turpentine, Resin, and Gum from the Gum Oleoresin of *Boswellia serrata*." *J. Ind. Inst. Sci.*, **4** (1921), 27.

4—Georges Dupont, "Acid Constituents of Pine Resin, *d*- and *l*-Pimaric Acid." *Compt. rend.*, **172** (1921), 923

5—G. Dupont, "Composition of Pimaric Acid." *Ibid.*, **172** (1921), 1184.

6—G. Dupont, "Isomerization of the Pimaric Acids." *Ibid.*, **172** (1921), 1373.

7—J. I. Simonsen, "Constituents of Indian Turpentine from *Pinus longifolia*." *J. Chem. Soc.*, **117** (1920), 570.

8—S. A. Mahood, "Thermal Decomposition of Turpentine." *J. Ind. Eng. Chem.*, **12** (1920), 1152.

9—A. Luttringer and A. Dubosc, "Preparation of Bornyl Formate." *Bull.* [illegible] *ind. Rouen*, **48** (1920), 81

10—A. Luttringer and A. Dubosc, "Action of Formic Acid on Dry Pinene Hydrochloride." *Ibid.*, **48** (1920), 84

11—A. Dubosc and A. Luttringer, "The Preparation of Camphor from Oil of Turpentine by Means of Salicylic Acid and an Alkaline Peroxide." *Ibid.*, **48** (1920), 85.

12—A. Dubosc and A. Luttringer, "Preparation of Bornyl Formate by the Action of Sodium Formate and Powdered Zinc on Solid Pinene Hydrochloride." [illegible] **48** [illegible]

13—A. Dubosc and A. Luttringer, "Preparation of Bornyl Formate by the Action of Sodium Formate and Iron Filing on Solid Pinene Hydrochloride." [illegible] **48** [illegible]

14—A. [illegible] Preparation of the Bornyl Ester of Propionic, Butyric and Salicylic Acids." *Ibid.*, **48** (1920), 88.

15—A. Dubosc and A. Luttringer, "Preparation of Bornyl Esters and Camphor from Oil of Turpentine, Propionic Acid and an Alkaline Peroxide." *Ibid.*, **48** (1920), 89.

16—A Luttringer, "Synthetic Camphor." *Ibid.*, **48** (1920), 90.

17—L. G. Wesson, "Conversion of Pinene Compounds into Isobornyl Ester and Camphane Mixture." U. S. Patent 1,372,382 (March 22, 1921).

18—E. Witte, "Camphor Synthesis according to Patent Literature." *Chem. Ztg.*, **45** (1921), 118.

19—Fab. de Prod. Chim. de Thann et Mulhouse, "Preparation of Borneol." Brit. Patent 144,604.

20—A. Pariselle, "Composition of French Oil of Turpentine and α-Pinene Bromide." *Compt. rend.*, **172** (1921), 1496.

21—G. G. Henderson and J. K. Marsh, "Action of Hypochlorous Acid on Pinene." *J. Chem. Soc.*, **119** (1921), 1492.

22—L. Ruzicka and H. Trebler, "Constitution of Nitrosopinene and Its Transformation Products." *Helvetica Chim. Acta.*, **4** (1921), 556.

23—J. J. Hofman, "Determination of the Separation Temperature of Essential Oils and Alcohol as a Criterion of Purity." *Pharm. Weekblad*, **57** (1920), 651.

24—A. Allina and H. Salvaterra, "Estimation of Benzine in Turpentine." *Chem. Ztg.*, **44** (1920), 673, 697.

25—H. Salvaterra, "New Methods of Examination of Turpentine Oil." *Ibid.*, **45** (1921), 133, 150, 158.

26—V. E. Grotlisch and W. C. Smith, "Detection and Estimation of Coal-Tar Oils in Turpentine." *J. Ind. Eng. Chem.*, **13** (1921), 791.

27—P. H. Walker, Chairman U. S. Interdepartmental Committee on Paint Specification Standardization, "Recommended Specifications for Turpentine." *U. S. Bur. Stds., Circ.* **86**, February 16, 1920.

28—F. P. Veitch and V. E. Grotlisch, "Turpentine: Its Sources, Properties, Uses, Transportation and Marketing." *U. S. Dept. Agr., Bull.* **898**, November 8, 1920.

29—Anonymous, "Various Methods of Augmenting the Energy of Hypochlorites." *Textile Mercury*, **63** (1920), 63.

30—Wm. B. Pratt, "Sulfur-Terpene Compound." U. S. Patent 1,349,909 (August 17, 1920).

31—L. Lewin, "Poisonous Extraction Media for Fats, Waxes, etc." *Z. deut. Ol- Fett-Ind.*, **40** (1920), 421, 439.

32—A. J. Virtanen, "Relation of Retene to the Resin Acids." *Ber.*, **53B** (1920), 1880.

33—O. Aschan, "Pinabietic Acid, a Homogeneous Resin Acid. I—Occurrence and Purification of the Acid." *Ann.*, **424** (1921), 117.

34—O. Aschan and K. E. Ekholm, "II—Molecular Weight and Rotatory Power of Pinabietic Acid." *Ann.*, **424** (1921), 133.

35—A. I. Virtanen, "III—Constitution of Pinabietic Acid." *Ann.*, **424** (1921), 150–215.

36—O. Aschan, "New Constituents of Rosin, the Colophenic Acids." *Ber.*, **54B** (1921), 867.

37—W. Fahrion, "On Colophenic Acid." *Ber.*, **54B** (1921), 1944.

38—O. Aschan, "On the Colophenic Acids. An Answer to W. Fahrion." *Ber.*, **55B** (1922), 1.

39—A. Grün, "Constitution of the Resin Acids of Colophony." *Z. deut. Ol- Fett-Ind.*, **41** (1921), 49.

40—E. Stock, "Chemical Constitution of American Rosin." *Farben-Ztg.*, **27** (1921), 156, 221, 287, 353, 416.

41—H. Wolff, "Detection of Rosin and Its Derivatives in Oil Varnishes." *Ibid.*, **26** (1920), 648.

42—D. J. McNicoll, "Estimation of Resin Acids in Fatty Mixtures." *J. Soc. Chem. Ind.*, **40** (1921), 124T.

43—R. Jungkunz, "Rosin in the Soap Industry." *Seifensieder-Ztg.*, **48** (1921), 563.

44—F. Goldschmidt and G. Weiss, "German Long Needle Pine Rosin." *Z. deut. Ol- Fett-Ind.*, **41** (1921), 81.

45—F. Goldschmidt, "Change in Powdered Rosin by Action of Air and Moisture." *Ibid.*, **41** (1921), 147.

46—R. Thindon, "Rosin Size Industry." *Papier*, **23** (1920), 145.

47—J. Traquair, "Colloidal Rosin in Beater Sizing." *Paper*, **26** (1920), 185.

48—E. Sutermeister, "Rosin and Rosin Sizing." *Ibid.*, **27** (1920), 22.

49—R. Sieber, "Rosin Sizing." *Zellstoff u. Papier*, **1** (1921), 15, 65.

50—C. C. Schneider, "Rosin or Engine Sizing." *Paper Trade J.*, **72** No. 18 (1921), 48.

51—G. W. Miles, "Oxidizing Resin." U. S. Patent 1,401,348 (December 27, 1921).

52—H. A. Gardner and R. E. Coleman, "Production of Rosin-Tung Esters in the Open Varnish Kettle." Paint Mfrs. Assoc. of U. S., *Spec. Circ.* **101**, August 1920.

53—W. F. Sterling, V. E. Grotlisch and F. P. Veitch, "Process for Making Varnish Material." U. S. Patent 1,395,874 (November 1, 1921).

54—A. Murray, "Hardened Rosin and Resin Esters." *Chem. Met. Eng.*, **25** (1921), 473.

55—G. Jahn, "Supersaturated Solid Solutions in Mixtures of Wax and Colophony." *Kolloid chem. Beihefte*, **13** (1921), 213.

56—L. Gerstacker, "Distilled Rosin." *Farben-Ztg.*, **25** (1920), 1170.

57—J. Hübscher, "Swedish Rosin Oil." *Seifensieder-Ztg.*, **48** (1921), 231.

58—L. P. Shippen and E. L. Griffin, "Pine Oil and Pine Distillate Emulsions." *U. S. Dept. Agr., Bull.* **989**, October 7, 1921.

** U. S. Pub. [illegible] *Rept.*, **30**, No. 41 [illegible], 3004

A Department Store Laboratory

By E. B. Millard

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PERHAPS it is because the chemist has been such a poor salesman of his services, even though he is working in a productive field where he should be of great value to his employer, that so few department or retail stores have chemical laboratories of their own, or regularly seek the advice of a chemist as to the quality of the merchandise they buy. Nearly all such stores have college-trained mechanical or architectural engineers in charge of their engineering problems; all of them have specialized advertising men. Yet neither the mechanical features and attractiveness of the building and its contents nor the selling value of advertising is nearly so important as a reputation for handling *all the time* a dependable line of goods. Such a reputation depends upon the ability of the buying staff to judge merchandise; but "judging" as applied to materials is practically a matter of the "feel" of materials, a mixture of intuition and previous experience with other similar material which has given more or less satisfaction. When stocks are to be maintained steadily at certain standards, especially if this must be done by purchasing from several sources, these standards should be carefully defined in terms of measurable quantities, and deliveries of merchandise checked constantly to see that they meet the established standards. The merchant who really *knows* his goods are all wool, or all silk, fast to perspiration, and of a specified weight or strength, consults a chemist constantly. Unless facilities for testing are constantly and quickly available, it is a rare merchant who will not take his chances or accept the word of a salesman as to what he buys to sell to his customers. Yet his reputation as a dealer in reliable merchandise, the good will of his trade, is at stake on every sale he makes.

E. B. Millard

The writer has been for some years in charge of a chemical laboratory maintained in a department store as an aid to its buying staff in the selection of supplies for its own use and for sale to its customers. The testing facilities of the laboratory are available without charge to any buyer who wants them; the laboratory has no authority over any purchases on which it passes. It gives an opinion as to the percentage of wool or silk, based upon an analysis of a sample, or as to the fastness of a color, or the probable wear to be expected of a material of a given mechanical strength. The buyer may or may not be guided by this opinion. When goods of any kind are purchased from a sample, it is customary for the buyer to send a specimen of the material delivered to the laboratory, where comparative tests are made for him to see if the delivery is of the same grade as the sample. Checking of this kind has often eliminated material from stock which would not have given the service expected of it.

It should be understood by all chemists, as it is not now understood, that to the layman there is no such thing as an organic chemist, a physical chemist, or a biological chemist. He is a Chemist, and he should realize the compliment implied by the capital letter; he should be far more ready than he is now to say, "I will find out for you," and less ready to say, "That isn't in my line." A department store chemist must be in addition an informal microscopist, a physicist of a kind, something of a skilled questioner, a laundryman when need presents itself, and an ever-ready consultant of the chemical literature to find out what is wanted. More often than not the questions presented to him are vague, poorly put, or indefinite; many times they do not concern what a chemist would call chemistry at all. But the man who comes to a chemist with these questions has faith in his science or he wouldn't come with the question. If the chemist can answer the question, or partly answer it, or even appear to be answering it while the conversation brings out what the other fellow is trying to ask in the first place, he has made a friend for chemistry. If he laughs at the question, or rules it out of the field of chemistry because he is too lazy to look it up, he might better give up chemistry and turn to a trade which is content to limit itself to that which is already known.

On the day our laboratory was installed, a boy came up from the wash dresses department and asked the chemist, "Can you analyze this dress for fading?" Ask yourself as a chemist, what you would have told him? Would you have asked him to leave it for a while and tried to find out for him, or would you have ruled that problem out of chemistry? The laboratory had a wash pan, a bar of soap, and hot water; with such "apparatus" the chemist "analyzed" the dress, dried it on a piece of string, took it to the alteration room and had it pressed. The color was the same as before and the dress showed an average shrinkage of 2 or 3 per cent in the half dozen places where it had been measured before and and after. To the man who sent up the dress that was an *analysis*, but "the separation of a substance, by chemical processes, into its constituents" (Webster) would have been a catastrophe. A chemist must daily choose his words very carefully, on account of such differences as between chlorates, chlorides, chlorites, etc., but he should remember that a questioner of nonchemical training knows hardly more than that a chemist performs in his laboratory a variety of mysterious operations which the outsider doesn't hope to understand, but which he thinks of as "analysis."

The ordinary work of a department store laboratory consists largely of determinations of the wool or silk in materials, and especially the detection of artificial silks, together with tests of the fastness of dyed fabrics to perspiration, sunlight, washing or water spots. For such service it is of tremendous advantage to have the laboratory located within the store building and immediately accessible to all departments by telephone or messenger boy at all times.

Most of the tests requested of such a laboratory are "rush" tests, but the laboratory also controls the deliveries of supplies of many kinds. A daily determination of ash and moisture in the coal affords a valuable check upon the quality delivered; determination of the butter fat in the milk and cream is also effective in its own way. There is a certain pride in saying, "Our own laboratory reports so and so."

When new materials appear upon the market, or new names are attached to modifications of old materials, the store laboratory is available at once to determine the composition of these materials and their suitability for the purposes to which they are put. Salespeople are provided with this information, so that they may answer promptly the inquiry of a prospective purchaser as to whether an article is of one material or another. Such service is important to a store, even if it only serves to keep out of stock articles which are of attractive appearance, but which may not be properly dyed or properly finished for outdoor wear, or which are not well chosen for their particular class of service.

One of the most important activities of a store laboratory is in connection with adjustments of claims of unsatisfactory materials. These claims occasionally arise from the abuse of materials, often innocently, by the customer; more often they are to be traced to the wrong use of materials or dyes in the manufacture of the goods, or to the defective material being made into a garment together with good material. In service the faulty fabric soon fails or a fugitive dye spreads or comes off on other clothing. It is the aim of the laboratory to trace the fault to its proper source, as a protection for the good name of the house, and as a service to the customer. If the customer has used bleach in the colored wash, or used corrosive toilet preparations, or used stockings as a pen wiper, the laboratory saves the store an expensive adjustment claim; if the lining of a suit or coat fades or crocks off on white clothing, or an undergarment gives way on its first washing it is the laboratory's place to report the probable cause to the proper person within the store, who recommends that adjustment be arranged with the customer.

In common with almost every chemist who has tried his hand at textile matters of any kind, our laboratory has designed a wearing machine. Doubtless a mechanical engineer would not approve of the details of the design, but it has been our experience that of two pieces of similar material, the one which will wear longer on our machine will wear longer in service. The plan is very simple: a canvas belt is driven at a speed of about six feet a minute from a wide faced pulley to which a revolution counter is attached, and the specimens under test are stretched over canvas-covered weights placed on the moving canvas belt. After many comparative tests we have found that a good coat lining should not wear through before a certain number of revolutions on the driving wheel; one which wears out in half the standard number is a poor lining. Perhaps this is not chemistry, and it is not much of a test anyway. The buyer of linings will, however, be content to call this test an "analysis;" and if by doing this for him we can pick out the better linings from the poorer ones we have raised the general standard of linings in the store. It will be chemistry to him, and it is through his opinions and similar opinions from others that the laboratory is left unmolested on the roof from week to week while it does hundreds and hundreds of tests which anyone would call chemical work.

At the time our laboratory was installed, the chief executive of the store confided in the writer that he was not sure why they were having a laboratory, but they were willing to bear the expense of [illegible] for a year or two as an experiment to see if it [illegible] benefit. Two or three items of a chemical program were outlined, but the main part of the list was left blank and for the future to develop. After four years the laboratory is handling over a thousand inquiries a month upon almost every activity of the store except the two or three in the original plan. Many of these are very informal, the kind of test one might make Saturday afternoon on a tiny piece of cloth clipped from the inside of a coat where it wouldn't show. An unspecified number of the rush tests (together with some of the more deliberate ones also, no doubt) have been incorrect, but the large majority of them have unquestionably been of benefit in the selection of materials about to be purchased, or in confirmation of the stock already on hand.

It seems probable to the writer that many retail stores will sooner or later find it to their advantage to maintain their own small laboratories, with simple equipment and two or three men, or a man and a boy, as a service to their staff and their customers. It will be many years in the experience of an active store laboratory before surprises are not of almost daily occurrence. The recent splendid improvements in the manufacture of artificial silks have made its distinction from real silk more and more difficult; the dyes used in most "novelty goods" will probably always require closer inspection than the stable colors in more common use; and the ever-increasing variety of finishing processes will unquestionably need some watching through chemical eyes.

A Metric Dozen

It has been observed that objection is being offered by many retail merchants against the metric system of packing. Contention is made that it is more convenient to buy "By the Dozen" than "By the Box of Ten" or "By the Carton." It is true that the carton does not specify any certain number, and equally true that long usage has made the dozen an easy term to think by, hence the reluctance to adopt any system that does away with such a convenient term. Those of us who would hasten the universal adoption of the metric system would undoubtedly further the cause a little by adopting some term as a standard to designate "a package containing ten articles"—a metric dozen.

The word "Dekon" is suggested as such a term. It is expressive, easily remembered, easily abbreviated as "Dk.," and if adopted and used by manufacturers now using the metric system of packing, and given notoriety through the press, would soon displace the "dozen" and score another point for "Metric," and others would no doubt soon see the wisdom of falling in line. "Methanol" was adopted almost over night, even by the laity. The Dekon could be made the standard small package, and ten Dekons, or a multiple thereof, depending upon the size of the article, a standard "case." The druggist could, with just as much ease, say "Send me down three dekons of helanthyol at once" as "three dozen" of the same article, and he would unconsciously be using the metric system. [*W. Carl Matthews*, Jacksonville, Fla.]

Commercial Methods of Making Carbon Black

In commercial practice there are four different processes of manufacturing carbon black from natural gas, states the Bureau of Mines in a recently issued bulletin. Classified according to the quantity of carbon black produced, these are: (1) Channel process; (2) small rotating disk process; (3) large-plate process; and (4) roller process. These methods differ mainly in the size and shape of the surface upon which the carbon is collected and the rate of travel of the moving devices. The channel process is probably the best method and is the one most extensively used. At present the production of carbon black by cracking or thermal decomposition methods is not extensive.

The French Senate has unanimously voted 2,000,000 francs for the observance of the hundredth anniversary of the birth of Louis Pasteur, this year. In voting the appropriation, Pasteur was described as the "symbol of French science."

Potash in America—Two Years' Progress

By John E. Teeple

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Production

SUCH PROGRESS as we have to record is not in increased production. In 1915 our production was practically nothing; in 1918 it reached a maximum of 54,000 tons of K_2O; in 1919 it was 32,000; in 1920 it was 48,000; and in 1921 it amounted to about 8000 tons from less than 20 plants.

To-day, in July 1922 as I write this, only one commercial plant is in full operation making potash as a main product. This is the American Trona Corporation plant on Searles Lake in California. Incidentally, this company has probably spent more time and money on systematic and fundamental research and development work than any other, which may account for its being in operation.

The by-product plants in commercial operation include the molasses distilleries, of which the U. S. Industrial Chemical Company is probably the chief producer, the cement plants and blast furnaces, the Santa Cruz Portland Cement Company in the lead, and the sugar companies using the Steffens process. That is about the whole story of production in America to-day. Of the 128 plants reporting production in 1918, over 100 made nothing in 1921. Some few were abandoned as war babies that could not live in peace times, but many are simply standing by continuing the study of their problems and hoping for Congress to give them the temporary protection that will carry them over this distressing period and enable them to make a permanent potash industry here.

John E. Teeple

The year 1921 was the worst we expect to see in potash production. The outlook for 1922 is better. The American Trona plant alone, although it only recently reopened, should produce more in 1922 than all America did last year. It has already exceeded 50 tons of K_2O per day and in September, after some minor troubles are worked out and a third smaller unit is in operation, it should be going at a rate of 22,500 tons of K_2O per year, or over 60 tons of K_2O per day. This is equivalent to about the output of the three largest German mines, or 5 average-producing mines, or 15 to 20 small ones.

Possibilities

Mention should be made of some nonoperating plants which look promising. The Eastern potash plant to operate on New Jersey greensand has been in construction several years, represents a large amount of money, and is not yet finished. Little idea can be formed regarding its position in a permanent industry until it has an operating history back of it. The plant and the hopes of its owners have been repeatedly described.[1]

None of the plants in Nebraska are now operating commercially, but some of the companies are understood to have given careful thought to their problems in recent years. Their particular hope of success lies in recovering soda ash and other by-products. Cheap fuel is also a necessity here and an oil well is now being put down to furnish it. The Nebraska lakes have been fully described[2] and there is no doubt that they will play an important part in permanent production.

The alunite beds of Utah have been receiving a good deal of attention from both promoters and technical men. The manufacture of potash and alumina or aluminium salts from alunite is a perfectly feasible operation. When someone is willing to spend the time and money necessary to get systematic information and work out manufacturing details this should be a real part of our industry. If anyone has done this up to the present it has not become a matter of public knowledge. The prospectuses that happened to be presented to me so far have consisted of partial information and half-baked details. One large company seems to be making real progress.

The story of Wyoming leucite is much the same as that of alunite. Leucite is a proper source of potash, and one company seems to be making real headway in the solution of the problem.

The Inyo Chemical Company of Deep Springs Valley, Calif., has had a pilot plant working on a natural potash brine at that place. The method is refrigeration to remove sulfate, then concentration by evaporation. They announce that the experiments have been successful and that they are now constructing a 10-ton per day plant.[3] Other natural brines rich in potash could be worked if people would study them.

Texas potash deposits have received as much newspaper publicity as a prima donna. No doubt soluble potash is there but no one seems to know whether it exists in commercially workable quantities. There is no reason why it should not and we certainly hope it does. Under the method of taking samples with core drills outlined by the Bureau of Mines, future oil wells will serve as prospect holes for potash and in a short time we will know just what we have to expect from Texas.

Development Work

Something of the progress made by nonoperating companies has been previously mentioned. Of more interest, however, is the development of the ones who have already succeeded, who are now working. A typical statement of the problems encountered in a by-product potash plant and a successful solution of the difficulties is found in the description of the Santa Cruz Portland Cement Company's methods.[4] Given 35,000 cu. ft. of gas per min. at 750° C., containing five lbs. of K_2O and a lot of other material that you do not want, how would you recover the potash at a profit?[2] If you are interested, read the solution in their article.

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[1] *Sci. American*, July 16, 1921; This Journal, **13** (1921), 693; *Chem. Met. Eng.*, **25** (1921), 1056.

[2] *Am. Fertilizer*, April 23, 1921.

[3] *Chem. Met. Eng.*, **26** (1922), 1034.

[4] *Ibid.*, **25** (1921), 316.

The problems of a brine working plant, like that of the American Trona Corporation, were described last year.[5] Progress since that report has been good. Equilibrium study of the system sulfates, chlorides, and carbonates of sodium and potassium between 20° and 100° has been completed for our purpose. Other equilibrium studies have included borax, metaborate, carbonate, bicarbonate, and other combinations. Of some scientific interest is the discovery by Mr. W. E. Burke of still another double salt, $Na_2B_2O_4.2NaCl.4H_2O$, to which he has temporarily given the euphonious name of "teepleite." Some practical applications of these studies have been: (1) An improvement in the grade of potash produced (for the last two months the product made has not in any week dropped below 95 per cent of KCl and several weeks has reached 98 per cent); (2) increase in the percentage of potash recovered; (3) simplified method of making borax; and (4) cheap and simple method of making boric acid.

Work on the other difficulties has been equally successful. Foaming in the evaporators has been entirely under control for a long time. The presence of borax as an impurity in potash has not been a problem for nearly three years, in spite of the fact that our friends, the recent enemy, are still talking about it. Dr. Whitney, Chief of the Bureau of Soils, recently issued another official statement on the high purity of American potash to counteract their propaganda, and agricultural experiment stations all over the country have been doing the same thing. It is amazing how many restatements of truth it takes to kill one lie.

Other improvements in evaporating, cooling, handling, and control have all reduced production costs. Much research work is under way, directed toward recovery of other valuable products from Searles Lake, and this is progressing favorably.

Cost and Market

Potash is one of the very few materials that is cheaper now than it was before the war—64 cents per unit to-day compared with an average of about 80 cents formerly. Converted to marks, this is about 330 marks to-day compared with 3.3 marks in normal times. The German workman used to receive 3.50 to 5 marks ($0.84 to $1.20) for a day's work. Now he receives 150 to 300 marks, say, 30 to 60 cents. In marks his wages have been multiplied by 50, while the price of potash has been multiplied by 100. In dollars he receives less than half what he did before, and works a whole day for what the American workman receives per hour. It takes on the average 12 to 15 days' work in Germany to produce 100 units or one ton of actual K_2O. This sells here at $64 and the labor cost for the 12 to 15 days' work is about $6 or $7. In America we would pay for that same amount of labor about $40. As a matter of fact, the labor spent to produce a ton of K_2O in America is less than four days in a good plant. We can turn out four times as much potash per man-day as they do, but we pay the man eight times the price the German receives. This is bound to continue so long as the value of the mark is falling faster than the price of German labor in marks is rising. There will always be a discrepancy because the American workman demands and we want him to have a higher standard of living than any other workman. This is why the industry needs temporary protection now. It will continue to need it until the production costs can be cut still lower. If we had a standard by which we could measure cost in terms of man-days, power, and steam on an even basis, America could probably sell at a profit to-day at any price that Germany could. But with the American man-day costing 8 to 10 times what the German one does we are calling for temporary help.

Propaganda

In a review of this kind it should not be necessary to discuss propaganda and possibly it ought not to be done, but it is necessary and is going to be done. Last fall we were deluged with a series of interviews from bankers, college professors, and business men. All agreed that there was no American potash industry, never had been, and never would be, and anyway American potash was bad and dangerous and God had given Germany good potash and plenty of it. It was almost sacrilegious to consider any potash but the German. For such a wide diversity of men, none of them directly connected with potash, there was an astonishing unanimity in ideas, and even in words and figures used. One could almost believe the interviews were mimeographed in one office. Then some interviews from fertilizer men complaining of the impurities in American potash, and specifying borax and salt. At that very time the nitrate of soda they were using often contained more borax than any American potash, and the German potash they used frequently contained more salt than it did potash. Again, about June first, we find advertisements in papers like the *Rural New Yorker* and the *Louisiana Planter* still harping on borax in potash, apparently in the hope of influencing some poor ignoramus who had not seen the repeated official government denials that harm could come from American potash more than from any other. These advertisements were signed "United States Soil and Crop Service, Potash Syndicate." This name looks harmless and patriotic but it is the official name of the Propaganda Office for North America of the German Kalisyndikat.

I would not bother you with this recitation except that it is a part of the struggle for existence that American potash has been making for the last two years, and an appreciable amount of time of technical men in the industry has been consumed in combating just that kind of stuff.

Many of us hoped that with the departure of the Kaiser from German affairs God and His Providence would no longer be restricted to Germany, but might be allowed to operate elsewhere. But not so! Within a month, two German business men assured me that Germany had a world monopoly on potash which could never be taken away. God had given it to her and she could starve or feed any part of the world she chose. This is of course hard on America. Who put the potash in the Nebraska and California lakes, the Utah marshes, the cement rock and the molasses, the greensand, alunite, and leucite? Are they not as natural as anything the other side of the Rhine? And are they not more accessible, being on the surface instead of far underground? German propaganda is meant for the unthinking and the unthinking often swallow it, particularly if it is signed with what looks like an American name.

The Future

The foregoing is a picture of the American potash industry during the last two years as I see it. To be a large industry that will protect Americans against future high-priced potash it needs some support and encouragement now. Some part of it will live whether it gets that support or not, but may be not enough to be a real protection. These plants cannot start operation again suddenly if they are allowed to die now. It takes time and money, and money does not lightly reënter an industry that has been allowed to fail from lack of public support at a critical time. We will have a large industry if we support it now, and a small one whether it is supported or not.

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[5] This Journal, 13 [illegible]

The Fertilizer Industry

By **Wm. H. Waggaman**

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IN THE PURCHASE of no other commodity offered on the market to-day is the consumer more dependent upon chemistry to protect him against fraud than he is in the buying of fertilizer. Before the advent of state fertilizer control enormous tonnages of relatively valueless materials were sold at a high price on the basis of an attractive name, a rich brown color and a strong disagreeable odor, and even up to the present time certain brand names persist which give the impression that the product offered has peculiar properties or mysterious power rendering it particularly well adapted for giving bumper yields of special crops.

Chemical control was first inaugurated in this country by the Connecticut Experiment Station in 1876, and laws were passed requiring the fertilizer manufacturer to state on his containers the actual quantities of fertilizer ingredients present in his goods. The other experiment stations soon recognized the advantage of such regulations and chemical control is now in effect in almost every state, and the guaranteed composition of fertilizer mixtures are so constantly checked up in laboratories of the state chemists that it is practically impossible for an unprincipled manufacturer to perpetrate a flagrant fraud upon the consumer. Chemical control, therefore, has proved a boon both to the reputable manufacturer and his customer by forcing the dishonest dealer out of business and increasing the efficiency of factory and field practice. It has also educated the farmer so that he is more familiar with the actual value of the various fertilizer ingredients, and brands with alluring titles no longer have the same psychological effect as of old. He wants definite assurance and actual proof that "Excelsior" contains something more than excellent filler, that "Champion" has the substance to deliver a real punch in the field, and that "Black Giant" is backed up by something more substantial than an overpowering odor.

Up until the past few years, however, there was little tendency toward the use of high-analysis fertilizers, owing to two main causes: First, many farmers found it difficult to realize that bulk has little significance and that it was often poor economy to purchase a low-priced fertilizer; second, there were many low-grade materials which for a long time were considered suitable only for fertilizer purposes and though they had unquestionable value as soil amendments it was practically impossible to use them in large quantities for the manufacture of high-grade goods.

The Stimulus of War

Conditions, however, are now changing materially. The farmer has learned the significance of potash, nitrogen, and phosphoric acid, and realizes that more labor and expense are involved when he handles, hauls, and spreads fertilizers containing low percentages of these ingredients than when he uses smaller quantities of higher grade goods. The producer of low-grade organic ammoniates such as tankage, cottonseed meal, and rendered garbage, has also found that these materials are much more valuable and bring a higher price when put into stock food rather than into fertilizer, and so the withdrawal of large amounts of such products from the fertilizer market has caused the manufacturer to turn to other sources of nitrogen to make up this deficit.

It is a curious paradox, but perhaps a fortunate fact, that so many of the materials necessary in the manufacture of explosives and other instruments of destruction are equally important in the production of fertilizers, to which we must now look to help make up the deficit caused by the ravages of war. The world-wide conflict, either by draining our natural sources of fertilizer materials or by cutting off the supplies normally imported from abroad, stimulated chemical research on methods of producing potash, nitrogen compounds, and phosphoric acid as nothing else would or could. Therefore it may be said that while the recent advances in the production of fertilizers are largely due to chemistry, the rapidity of these advances we chiefly owe to war.

Potash Salts

Before the war the supplies of potash salts imported into this country from the enormous deposits in Stassfurt, Germany, were more than ample to meet our fertilizer requirements, and the price of these natural salts was so low that little encouragement was offered to develop methods of obtaining potash from domestic sources. Chemical processes for the production or recovery of potash from silicate rocks and organic materials were little known outside of the laboratory, and while patented processes for extracting this fertilizer ingredient from such sources existed the quantity thus produced was inconsiderable when compared to the enormous tonnage annually imported.

With the advent of war, however, conditions completely changed. Our chief source of potash was suddenly and completely shut off and the spectacular rise in the price of this material rendered it economically impossible to use more than the smallest quantities in mixed fertilizers. Even then the limited supplies on hand were soon exhausted and we were confronted with the possibility of a serious curtailment in our agricultural output.

Chemistry was called upon to help out in this real emergency and nearly every possible source of potash, both organic and inorganic, was given consideration and close study. The feverish energy expended in research was not long in bearing fruit. Substantial quantities of potash were extracted from the mineral alunite, of which we have large deposits in southern Utah. Improved processes for recovering this fertilizer ingredient from such organic sources as kelp and sugar-beet waste were devised. Chemical investigations established the fact that we possessed in our blast furnace and cement industries immense potential sources of soluble or available potash and the latter industry was soon contributing a considerable annual tonnage. Finally the recovery of potash from the brines of certain saline lakes in Nebraska and California was found to be economically feasible and when the armistice was signed a number of plants were turning out potash from this source.

Within four years an American potash industry was built up where none previously existed and in 1918 we turned out 50,000 tons of actual potassium oxide or about one-fifth of that normally consumed for agricultural purposes. While it is generally believed that this industry is not yet sufficiently firmly established to meet foreign competition unless it has a protective tariff, the potash producers claim that such pro-

[illegible] ly or until they have [illegible]ted or increased the efficiency of their chemical processes.

Whether or not the United States continues to produce a large tonnage of potash is an open question, but we have learned that we have resources of this fertilizer ingredient and in case of emergency we know where and how to get it.

Nitrogen Carriers

The production or recovery of compounds of nitrogen by chemical processes is one of prime importance to the fertilizer industry. Throughout the war difficulty of obtaining adequate quantities of fixed nitrogen caused the allied nations considerable alarm. None of the large nations, with the possible exception of Germany, was producing sufficient amounts to meet its requirements and the imports of Chilean nitrate upon which they were so largely dependent were always threatened by the menace of the submarine. The withdrawal of much of our supply of organic ammoniates for stock feeding purposes had already placed an added strain on our normal output of nitrogen products, and this, coupled with the sudden demands of war, brought us face to face with the danger of a shortage for fertilizer purposes.

In order to enhance our own nitrogen output every effort was made to increase our production of ammonium sulfate by the replacement of the old "beehive" coke ovens with the by-product type, and so vigorous and successful were these efforts that within a period of two years our output of this product was pushed from 197,128 tons to 348,654 tons annually. Thus an almost criminal industrial waste which had been going on for many years was materially reduced. Nothing but the emergency of war could have brought about this rapid increase in the recovery of the by-products of bituminous coal.

But our own supply of nitrogen products was still far short of that required. Moreover, the importance of making ourselves independent of foreign sources gave an added stimulus to researches for the synthetic production of nitrogen compounds from the inexhaustible supply in the air. The cyanamide process was the only one of these methods which had been commercially successful in America and this was not in operation in the United States. The knowledge and advice of the foremost chemists and technologists in the country were sought, and no effort and expense spared to solve this problem so vital to the public safety. While these investigations are still being continued, much progress has been made, particularly on the Haber process, of manufacturing ammonia, and there is little doubt that within the next decade we will be producing synthetic nitrogen compounds at a price sufficiently low to compete with the natural nitrate deposits of South America and the ammonium sulfate obtained from our by-product coke and gas plants.

Phosphoric Acid and Phosphates

While chemical processes were used in the manufacture of phosphatic fertilizers long before they were employed in the production of either of the other two fertilizer ingredients, it was not until about the middle of the last century that we advanced beyond the application of natural sources of phosphoric acid.

In 1840 Liebig and Lawes proposed treating bones and phosphate rock with sulfuric acid in order to render the phosphate water-soluble and more quickly available to crops. So successful has this simple chemical process proved that it is now almost universally employed, and fully 50 per cent of the sulfuric acid produced in this country is used in the manufacture of acid phosphate.

Basic phosphate [illegible] produced in 1875, and while merely a by-product obtained in the manufacture of steel by the basic Bessemer process, it has been a very valuable supplement to acid phosphate. The discovery of basic slag was largely due to an intimate knowledge of the chemistry of iron and a close study of the nature and properties of its impurities.

When war was declared the demand for sulfuric acid so increased that we were hard pressed to produce sufficient quantities for both munitions and fertilizer purposes, and this led to the investigation of other methods of producing soluble and available phosphates. The indications are that at least one of these general processes is going to play an important part in future fertilizer practice. The pyrolytic method of producing phosphoric acid, wherein mixtures of phosphate rock, silica, and coke are heated at high temperatures and the phosphoric acid distilled off and collected, has already proved commercially successful, and though most of the acid thus produced is consumed in the manufacture of baking powder chemicals and other relatively high-priced phosphate products, this process has so many advantages over the sulfuric acid method where cheap power and fuel are available that there is little question it will eventually be widely employed in the production of phosphate fertilizers. By the use of this process many deposits of low-grade rock that are considered unfit for the manufacture of acid phosphate will be made available, and the "run of mine" phosphate can be used directly without the expense and losses entailed in the washing and screening processes now so extensively employed. Moreover, the fact that the pyrolytic process yields a concentrated product which can stand the cost of long shipments may make it possible to develop more quickly our immense reserves of phosphate rock in the far west that have as yet been exploited to only a limited extent because of their distance to the fertilizer market. The success of this method, however, depends on close chemical control, and a careful study of the reactions that take place between phosphate of lime, silica, iron, and aluminium at high temperatures under both reducing and oxidizing conditions.

Concentrated Fertilizers

The trend of the fertilizer industry to-day is toward the manufacture and use of more concentrated products. While increased freight rates and higher labor costs are partially responsible for this movement, a better understanding of the chemistry of fertilizers and the economies effected by the employment of new and improved processes are the main causes for our advance. Along with the direct manufacture of phosphoric acid and the synthetic production of ammonia must come the wider use of definite and relatively pure chemical compounds for fertilizer purposes, for these two fertilizer ingredients must be combined with a base and an acid, respectively, in order to handle, ship, and distribute them successfully. The practice in the past has been to partially neutralize phosphoric acid with lime and to fix ammonia with sulfuric acid in the form of ammonium sulfate, but such procedure appears foolishly extravagant when we consider that neither of these materials adds anything to the value of the product. The logical procedure is to combine the phosphoric acid with ammonia to form ammonium phosphate or with potash as potassium phosphate, and where both ammonia and nitric acid are produced combine them to form ammonium nitrate. In every case a salt is obtained wherein both the acid and the base contribute their share to the market value of the fertilizer.

It is recognized, of course, that great care must be exercised in distributing such concentrated fertilizer compounds in the field, and it may be necessary or advisable to dilute such products before they are actually applied to the soil, but this can be done near the point of consumption and the needless expense of shipping inert or valueless material thus avoided.

While the manufacture of fertilizers has for many years shown a steady healthy growth, it is now rising from the plane of a big business conducted largely along "rule of thumb" lines to that of a true chemical industry founded upon sound scientific principles, which make for higher efficiency, greater economy, and better service to both the individual and the nation.

Developments in Nitrogen Fixation[1]

By J. M. Braham

Fixed Nitrogen Research Laboratory, Washington, D. C.

THE PROBLEM of cheaply obtaining nitrogen in forms suitably combined for use in agriculture, the industries, and in munitions is probably the most important one confronting the chemical industry at the present time. The dependence of the food supply of the world on combined nitrogen is well known; nitrogen compounds occupy an important place in the industries; and the very great importance of combined nitrogen from a military standpoint requires no explanation.

The use of the practically inexhaustible supply of free nitrogen in the atmosphere to supplement the inadequate natural sources of combined nitrogen is a development of the last twenty years. This relatively new industry of nitrogen fixation is undergoing rapid developments in many countries. In the present paper an attempt has been made to indicate the general lines of development, the progress and the present status of nitrogen fixation. In such a short article, however, only the most important developments can be considered.

Fixation Processes

Although a large number of processes for the fixation of nitrogen have been suggested and more or less thoroughly tried out, there are at the present time only three in successful commercial operation. These, in the order of their development, are the Arc, Cyanamide, and Direct Synthetic Ammonia (Haber). None of the other processes thus far suggested appear to give promise of commercial development in the very near future.

The Arc Process—The arc process is the oldest and in many respects the simplest, consisting essentially in passing air through a specially constructed electric furnace in which the union of nitrogen and oxygen is effected, and then absorbing the oxides of nitrogen in water. Important experiments in the early development of this process were performed by Bradley and Lovejoy at their plant at Niagara Falls in 1902–1904. The process was being developed at the same time in Norway by Birkeland and Eyde, and in 1903 they succeeded in starting the first successful industrial plant. No improvements of a fundamental nature have been made in this process since the early period of its operation. The changes that have been made from time to time have been largely limited to furnace design and operation, and the various present forms of the process differ only in these two respects.

The principal handicap of the process is the very large power requirement—about 67,000 k. w. h. per ton of nitrogen fixed. Its profitable operation is, therefore, limited to regions in which very cheap electric power, off-peak as well as continuous, is available. Another rather serious handicap is the low concentration of nitric oxide in the furnace gases, which results in high absorption and concentration costs.

Notwithstanding these difficulties, there are at present about twelve arc-process plants located in Norway, Switzerland, Austria, Germany, France, Italy, Canada, and the United States. Their combined maximum production capacity is, however, quite small, being approximately 36,000 metric tons per annum, which is only about 6 per cent of the world's total nitrogen fixation capacity. Norway, with her abundance of cheap water power, produces about 85 per cent of the total output of this process. The arc process plant of the American Nitrogen Products Company of Seattle is the only one in the United States. Its capacity is about 300 tons of fixed nitrogen per annum.

Although somewhat less than 2.5 per cent of the total energy input of the arc process is absorbed in nitric oxide formation, the possibility of drastic reductions in the power requirements by modifications, such as in furnace design, seems quite doubtful. It appears that the process in any of its present forms is essentially a thermal one, the main function of the electric discharge being to produce the very high temperatures that favor nitric oxide formation. From this viewpoint the thermal efficiency is probably much above 50 per cent, and hence the possibility of a large reduction in the power required seems doubtful. The possibility of finding conditions under which the actual energy input more nearly approaches the heat of nitric oxide formation is of course not precluded. Research on the nature of chemical reactions in other types of electric discharge, such as in the corona, may lead to the development of a much more efficient process. Such a process, however, would be of a very different nature from the present arc process.

In view of the exceedingly high-power requirements, the high cost of absorption and concentration of the product, and the fact that the process does not appear to offer possibilities of decided improvements, it seems improbable that the arc process in its present forms will continue to be an important factor in nitrogen fixation.

The Cyanamide Process—That nitrogen combines with calcium carbide, when heated to 1000° to 1100° C., to form calcium cyanamide, was discovered by Frank and Caro in Germany in the course of an investigation on the production of cyanides. Impetus was given to the development of this fixation process by the discovery that the crude product could either be used directly as a fertilizer or converted to ammonia simply by autoclaving.

The first commercial plant was operated in 1906, and following this the new industry grew rapidly. By 1913 there were about 15 plants with an estimated capacity of 300,000 metric tons of crude calcium cyanamide—or lime-nitrogen as it is frequently called—operating in nine countries. It underwent an enormous expansion during the war since it and the arc process were the only ones in operation outside of Germany. At the end of the war there were 35 cyanamide plants located in Germany, Austria, France, Scandinavia, Italy, Switzerland, Japan, Canada, and the United States. Their estimated total maximum production capacity at that time was 1,625,000 metric tons, corresponding to about 325,000 metric tons of nitrogen. Actual production to capacity was not reached, however, since a number of plants were just being completed when the war ended. It is understood that a number of these plants have since been dismantled. There is only one cyanamide plant in the United States. It is located at Muscle Shoals, Ala., and has a capacity of 40,000 tons of fixed nitrogen per annum.

The cyanamide process at the present time is in a comparatively high state of development, and therefore a decided reduction in the cost of fixed nitrogen by this process seems doubtful. In this connection it may be pointed out that since the cost of the raw materials, limestone, coke, and coal, are practically fixed, the possible economies in the process must come principally in the lowering of the energy requirements for carbide production and in increasing the efficiency of nitrification. Approximately [illegible] one ton of nitrogen by this process, and the efficiency of nitrification is about 85 per cent. The economies that might theoretically be achieved in carbide manufacture cannot be accurately estimated, owing to the present limited knowledge of the thermodynamics of carbide formation. From a rough calculation, however, it appears that the efficiency of the present-day carbide furnace is quite high, and hence a large reduction in the power cost of this process by improvements in carbide furnace practice seems improbable. No especially promising modifications of the cyanamide process have been suggested. A careful investigation into the thermodynamics and mechanism of carbide formation and nitrification, and the effect of various added materials on these reactions, might, however, lead to very important modifications of the process.

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[1] For a complete discussion of the nitrogen problem, with particular reference to the United States, attention is called to a recently published 350-page report entitled "Report on the Fixation and Utilization of Nitrogen," prepared by the Nitrate Division, Ordnance Office, War Department, assisted by the Fixed Nitrogen Research Laboratory, Department of Agriculture, on which the present brief summary is largely based.

The greatest advantage which the cyanamide process possesses over the other fixation processes lies in the extremely wide variety of products obtainable. Thus, in addition to calcium cyanamide, there may be obtained by transformation processes ammonia, nitric acid (by ammonia oxidation), cyanides, hydrocyanic acid, cyanamide, dicyanodiamide, urea, guanylurea, guanidine, biguanide, etc., and the very numerous derivatives of these latter compounds which are becoming more and more important in the manufacture of munitions, dyes, and drugs. Many of these important compounds, such as nitroguanidine, for example, cannot be furnished in quantity by any other process. Although the use of calcium cyanamide as a fertilizer is limited, it seems, however, that a well-rounded nitrogen industry must of necessity make provision for the production of calcium cyanamide.

The Direct Synthetic Ammonia Process—The fixation of nitrogen by direct union with hydrogen to form ammonia is the newest commercially successful process, and is the one that offers the greatest possibilities for further development. The equilibrium in the ammonia-synthesis reaction is such that the conversion to ammonia is higher, the higher the pressure and the lower the temperature. The upper pressure limit in this process is conditioned largely by the mechanical problems of equipment strength and the compression of large volumes of the gas mixture. The lower temperature limit is conditioned by the reaction velocity. The use of pressures as high as 1000 atmospheres in this process is now being investigated and the present lower practicable limit of temperature even when using an active catalyst is around 500° C.

The early development of this process was due to Prof. Fritz Haber, in Germany, and it is only in that country that the process has yet been operated on an extensive scale. The first commercial plant commenced operation in 1913 after many years of experimentation. The process experienced an enormous development in that country during the war, the present estimated production capacity being 300,000 metric tons of nitrogen per annum. The low power requirements of the process as operated in Germany, about 4000 k. w. h. per ton of nitrogen fixed, is probably one of the principal reasons for this exceedingly large expansion when compared with that of the other processes.

There are at present four lines of development of the direct synthetic ammonia process, which differ principally in the pressure employed, although the manner of gas production and ammonia removal also varies somewhat. These are: the American (General Chemical Company) process, operating at 100 atmospheres; the original German (Haber) process, at 200 atmospheres; the Italian (Casale) process, at 300 to 600 atmospheres; the French (Claude) process, operating at 600 to 1000 atmospheres.

As to the present development of these four forms, the extensive production of fixed nitrogen in Germany by this process has already been mentioned, the Italian process is now operating on a small scale, and the French process is in a semicommercial stage of development. The American form of the process is the development of the General Chemical Company. In 1917, a synthetic ammonia plant of 8000 tons rated capacity was constructed for the United States Government at Sheffield, Ala., based on the General Chemical Company's designs. The plant, however, did not operate satisfactorily and was closed down in the early part of 1919. In August 1921, the Atmospheric Nitrogen Corporation (General Chemical Company and the Solvay Process Company) began the operation of the first unit of their synthetic ammonia plant at Syracuse, N. Y., with a daily capacity of about 10 tons of anhydrous ammonia. It is understood that it is operating very satisfactorily. The design of this plant is essentially the same as that of the Sheffield plant but embodies the modifications which the trial operation at the latter plant had shown to be necessary.

Aside from the mechanical difficulties presented in handling large volumes of gas at very high pressures and at temperatures of 450° to 600° C., the two principal problems in the synthetic ammonia process are the production and purification of hydrogen and the development of an active and robust catalyst. The importance of the first of these is seen from the fact that in the Bosch method of gas production—which is used in Germany and, in a somewhat modified form, in this country—about 20 per cent of the total manufacturing cost is in hydrogen manufacture and a further 50 per cent in purification before it is suitable for passage through the catalyst. The exceedingly large cost of purification is largely occasioned by the fact that catalysts suitable for operation on impure gas at moderately low temperatures have not thus far been developed. The great opportunities for development along these lines through research are therefore quite evident.

The use of electrolytic hydrogen, whereby the cost of gas purification would be greatly reduced, is now being considered. The advantage gained in this respect, however, would in most countries be largely offset by the cost of additional power required (a total of about 18,000 k. w. h. per ton of nitrogen fixed).

The utilization of the waste hydrogen obtained in the electrolytic manufacture of oxygen, caustic alkali, etc., by installing small synthetic ammonia plants has been suggested. Chances of developments in this direction appear quite promising, particularly along the lines of the Claude process.

It is seen from the foregoing that the direct synthetic ammonia process is being very actively developed at the present time, and therefore a large expansion of the nitrogen industry along this line seems quite certain. Catalyst research will undoubtedly play a very important part in this development.

Future Possibilities of Nitrogen Fixation

The nitrogen fixation industry is to a certain extent now marking time, owing largely to the forced growth of the entire nitrogen-producing industry, including coke-oven ammonia, which was brought on by the war. Many of the war-built fixation plants are now unable to meet the competition by by-product ammonia and Chilean nitrate. Much is yet to be done, and much can be done, toward lowering nitrogen fixation costs. The problem is so large and so difficult, however, that many years may be required for its satisfactory solution.

While nitrogen fixation is undergoing but little expansion at present, there is a decided activity in many countries in nitrogen fixation research and development. The possibilities of fruitful research in nitrogen fixation and utilization are almost unlimited. Thus, research leading to further improvements in existing processes, the investigation of proposed but not fully tried-out processes, the discovery and development of entirely new processes, and studies on the transformation of nitrogen-containing compounds to render them suitable for the various needs in agriculture and the industries, presents most unusual opportunities. In view of the importance of the nitrogen problem and the vigorous manner in which it is now being attacked in many countries, the fixation of atmospheric nitrogen is certain to experience very important developments within the next decade.

Desulfurizing Coke

A study of the desulfurization of coke was begun July 1922, at the Experiment Station of the United States Bureau of Mines, Pittsburgh, Pa. This is a practical follow-up of the theoretical study of the oxidation of iron sulfate in the coke and the subsequent removal of the free sulfur formed by this oxidation. Literature on this subject is being reviewed. Many patents were taken out in the years 1850 to 1870 and few since. Roasting and steaming were favorite methods. In this connection, methods for converting sulfur in coke into the FeS form are being sought. A process based on such method would hold back sulfur that might ordinarily be evolved, then this sulfur could later be removed by oxidation together with much additional sulfur. It seems that Fe_3O_4 mixed with coal being coked decreases the sulfur in solid solution.

Progress in the Canning Industry in the Last Ten Years

By W. D. Bigelow

Director of Research Laboratory, National Canners Association, 1739 H St., N. W., Washington, D. C.

THERE are perhaps two distinguishing features of the canning industry of the present decade: First, coöperation of effort, and second, fundamental and systematic study of the principles on which the industry is based.

Harris and Ewing

W. D. Bigelow

During this time the idea of trade secrets in technological operations has disappeared from most branches of the canning industry and technological questions are now discussed freely. This policy has resulted in a greatly improved product, and has made it possible to define within broad limits the information of the industry regarding technological processes and to point out more definitely than was heretofore possible the needs of the industry for improvement in those processes.

Raw Products

It has become evident that canning is intimately connected with agriculture, and that its future success must depend in large manner on the success of growers in producing canning crops. Increased attention has been given to the development of varieties which yield abundantly and, at the same time, possess the characteristics most desired for the production of canned foods. The importance of planting seed that is true to type and which may yield an abundant harvest under satisfactory growing conditions is now generally appreciated.

Canning Machinery

The last decade has seen the perfection and general use of machines that had been relatively imperfect as well as the development of new machines for operations previously conducted by hand. As a result of the developments in canning machinery, it is now possible to handle many products almost entirely by machine, thus securing greater uniformity, reducing the cost of manufacture, and contributing largely to the sanitation of the canning plants. This improvement in canning machinery is general and applies to nearly all products packed. The following are mentioned merely as illustrations of the progress that has been made in this field:

Corn huskers have come into universal use, and cutters have been so developed that the corn is removed from the cob in a much more satisfactory manner than was formerly possible.

Blanchers have been so developed that they can be used more generally, and many products, such as pumpkins and beets, are now blanched in continuous machines.

Washing machines for preliminary cleansing of all manner of raw products have been brought to a high stage of perfection.

Filling machines for filling the raw product, such as peas and beans, into the cans, have been improved so that the cans may be filled more uniformly and with less mutilation of the product.

Automatic conveyors for the raw product, the empty cans and the filled cans have been highly developed, and greatly facilitate the transportation between different portions of the plant. This improvement in conveyors is advantageous in many ways. It cheapens the cost of production, hastens the operation of canning with a resulting increase in quality, and contributes largely to the general cleanliness of the plant.

Research Laboratory

As a result of the coöperative spirit already mentioned, the canning industry nine years ago established a research laboratory which might serve as a center for studying the fundamental principles of canning technology. In this laboratory it is possible to study the general problems of the industry more adequately than could be done in a laboratory maintained by a single interest. In addition to general problems, the laboratory receives many complaints and inquiries from individual canners, together with their observations regarding the same. Such communications are often accompanied by samples for inspection or analysis and are frequently followed by experimental work at the canning plant. Collaboration is also received from allied industries, and often with governmental agencies.

Tin Plate and Cans

During the last ten years we have really begun to understand the desiderata in tin plate intended for packers' cans. We have learned that increasing the weight of coating does not increase the amount of tin dissolved by certain foods, as was formerly believed by many to be the case. On the other hand, increasing the weight of coating does materially reduce the number of perforations and consequently the amount of loss experienced with certain fruits. A substantial beginning has also been made in the study of steel intended for the manufacture of tin plate.

During this time the sanitary can has been developed to such an extent that its use with vegetables processed at high temperatures has become practicable. As a result, the sanitary can has practically superseded the old hole-and-cap can, thus affording a package which not only reduces the cost of operation but enhances the quality of the product.

Processing of Canned Foods

The characteristic feature of canned foods is that they are placed in hermetically sealed cans and sterilized by heat.

The times and temperatures of processing were entirely a matter of experience, and it was only within the last five years that a systematic study of the fundamentals of processing was inaugurated. This investigation includes: First, the study of the penetration of heat to the center of cans of various kinds of foods; second, the hydrogen-ion concentration of canned foods and the influence of the canning process on the hydrogen-ion concentration of the product; third, the study of the thermal death point of resistant bacteria isolated from spoiled canned foods; and fourth, the correlation of the results of the three separate studies just mentioned and the calculation from the data afforded by those studies of the theoretical time necessary to sterilize various foods at any particular temperature. This theoretical process time is then available for guiding experimental packs of cans of various products inoculated with resistant bacteria. In this way the processes of the canning industry are being studied and the results already obtained have been found of substantial value in guiding process temperatures and times.

Quality and Appearance of Canned Foods

The improvement in canning machinery previously commented upon has contributed to the improvement in the appearance of the product packed. The proportion of canned foods of high quality is materially higher than it was ten years ago. In many products the highest grade packed also shows a marked improvement, and there is a corresponding improvement in the lower grades. The increase in quality consists both in appearance and in flavor. It is the result of a general movement to bring the raw product to the canning plants in better condition and to handle it by more prompt and more efficient methods. In keeping with the increased quality is a pronounced tendency among canners to so label their product that consumers can have more accurate knowledge of the exact nature of the contents of the can. The improvement in this direction is not yet generally appreciated. Grades are hard to describe, and it is difficult to so word a label as to give the consumer all of the information which he should have. Systematic progress in this matter is being made, however, and various grades are gradually being defined so that a change in labeling will be possible.

Sanitation

In many of our foremost plants careful attention was always given to questions of sanitation. Many difficulties were encountered in such plants, however, because of the inherent sloppiness of many of the operations and the ineffective machinery and system of conveyors formerly available.

Improvements in these directions and in ideas of plant construction have greatly changed the sanitary condition of the best plants. In many plants a striking change of sanitary conditions has been made. The adoption of sanitary machinery and conveyors and the improvement in quality and appearance of the product have contributed to the general movement of improving the surroundings of the canning plant. This is especially evidenced by increased light and cleanliness within the plant itself and more efficient removal of waste products.

A Boom Needed

By H. W. Jordan

133 Stolp Ave., Syracuse, N. Y.

The presidents of three great American universities in addressing their graduating classes struck a common note of warning which university men of the chemical and engineering industries will do well to heed. At Yale, President Angell urged that educated men lead public action against the prevailing swift current of lawlessness and selfishness. At Harvard, President Lowell deprecated the tendency to float with the crowd. He urged growth of the American pioneer spirit that has characterized us as a people creative of great achievements, both material and spiritual. President Hibben of Princeton said, "We are all aware of the fact that there is something wrong with the world. If you think that it is going to the devil, I rejoice in that belief, because I know that there naturally will arise the determination that you, for one, will do everything in your power to prevent it."

The close agreement of these intellectual leaders in their analysis of the idea which they considered most important to impress upon the minds of graduating seniors is no mere accident. Their joint conclusion that there is too much complaisant drifting with the crowd—too little creative thinking by university men as citizens—deserves serious consideration by everyone of scientific training. Clear appreciation of the close relation between the industrial processes of the chemist or engineer and the social economic situation is arising. Edwin Grant Conklin, Arthur Pound, James H. Robinson, Lothrop Stoddard and other far-sighted men of creative mind, who do not drift with the crowd, see that industrial stagnation, high cost of food and housing, coal strikes and the like are ultimate effects, and not primary causes. These thinkers throw the spotlight of science on the waste of energy spent in fighting effects—energy which should be used to discover and correct causes. They show the absurdity of trying to bring the millennium upon earth by means of the revised statutes. The most recent example of this triumph [redacted] the Constitution [redacted] amendment *ad infinitum* "to meet the needs of the people."

This sublime example of trying to balance oneself by the extended left arm with hand gripping the back of a kitchen chair supported by one leg on the top end of a thirty foot pole whose lower end rests on the chin of Congress impels one to rush for the net before gravity gets a start on the wabbly column.

Members of the American Chemical Society need to organize a salvage corps in behalf of engineering industry and of their individual selves for study and action upon the newly discovered relationship between modern, automatic machine industry and the social structure. "You, for one, need do everything in your power" to promote such biological, industrial research. Discussion of the writings of Professor Conklin and his associates—for example, of his article on the "Future of Evolution," in the July *Yale Review*—would be a stout boom thrown across the river of popular thoughtless clamor for national laws designed to regulate us from breakfast to bedtime; a boom behind which many millions of valuable mental, social timber would be impounded for constructive use.

Will you, "for one," help lay that boom?

Help Kazan

Many chemists are deeply interested in the plight of their colleagues abroad and have contributed generously to their relief. Here is a real opportunity to help where help is sorely needed, and through the American Relief Administration we know the utmost economy and efficiency are secured. Read this letter sent to a member of our Society.

Dear Sir:

I take the opportunity to send you my scientific works through the American Relief Administration which is affording now great help to the starving population in the Volga district.

The great war, the revolution, and the civil war in our country did not allow me to send you my works earlier.

Unfortunately the difficult economical situation in our country does not allow us to carry on our work regularly. We are now obliged to spend our physical and mental strength in searching ways of getting foodstuff for ourselves and our families.

We send you and all American chemists our friendly regards, and we beg you all to help the professors and assistants of chemistry of the Kazan University and of the Kazan Technological Institute by sending them food through the A. R. A.

I hope that our scientific works in chemistry, though modest, give us the moral right to send to all our American chemist friends this prayer. The relief received will give us the possibility to regain our physical and mental strength and to continue to work for the science.

Respectfully yours,
Alexander Arbusoff,
Professor of Organic Chemistry

Kazan University
Kazan, Russia
May 16, 1922

Recent Chemical and Technological Advances in Our Knowledge of Gelatin and Glue

By **Robert Herman Bogue**

Industrial Fellow, Mellon Institute of Industrial Research, Pittsburgh, Pa.

THE PAST few years have witnessed advances of a truly startling nature in almost every branch and subdivision of theoretical and applied chemistry, and the chemistry of gelatin has not lagged behind in this forward sweep. The gelatin ionogenic equilibria and their consequences have been studied from many angles[1–31,*] by Loeb, Smith, Sheppard, *et al.*, Kuhn, Miss Lloyd, Procter, *et al.*, Pauli, Davis, *et al.*, Fischer, Bancroft, Bogue, and others. Theories of the structure of gelatin, or of elastic gels in general, have been discussed by Bradford, Hatschek, Barratt, Miss Lloyd, Zsigmondy, Robertson, Fischer, Bancroft, McBain, *et al.*, Holmes, Sherrer, Loeb, and Bogue. Analytical data upon the composition have been accumulated by Dakin, and by Bogue. Still other aspects of the question have been presented by Alexander, Elliott and Sheppard, Thomas, Seymour-Jones, Mees, and others. Lastly, as an index of the awakened interest in gelatin and glue, books are in press or being prepared upon this subject by Sheppard, Alexander, Thiele, and Bogue.

R. H. Bogue

Ionogenic Equilibria

The work which stands above all others in this field is the very important series of investigations by Jacques Loeb.[1] His accomplishments appear to be two in number: First, the protein colloids, as gelatin, casein, egg albumen, etc., are shown to be amphoteric bodies whose general behavior is explainable by an application of the classical laws of electrolytic dissociation and valency; and, second, the special colloid behavior of these bodies and the degree of such action are shown to be determined by an application of the Donnan membrane potential law.

Gelatin is found to exist in three states: as non-ionogenic or isoelectric gelatin; as a metal gelatinate; and as a gelatin salt. At one definite hydrogen-ion concentration, namely, $10^{-4.7}$ N, or pH 4.7, gelatin can combine with neither anion nor cation and is un-ionized. At a pH greater than 4.7 it can combine only with cations forming a metal gelatinate, as sodium gelatinate, and at a pH less than 4.7 it can combine only with anions forming a gelatin salt, as gelatin chloride.

Loeb has more recently shown that the swelling, the viscosity, and the osmotic pressure effects produced by varying the ionogenic equilibrium may be adequately explained and predicted by an application of Donnan's membrane potential law.[32] By calculating from Nernst's formula for concentration cells at 24° C.,

$$\text{p. d.} = 0.059 \log \frac{C_1}{C_2},$$

where p. d. is the potential difference between the two solutions in which C_1 is the H-ion concentration inside the gelatin solution and C_2 the same in the outside solution (separated by a semipermeable membrane). By comparing the observed and the calculated p. d. from the measurements of pH in the two solutions, Loeb obtained very satisfactory concordance. Procter and Wilson[6] had previously made use of the Donnan equilibrium to explain the swelling of gelatin.

The viscosity of two-phase systems has been studied by Hatschek,[33] who calculated formulas to cover the two main conditions of loosely packed and closely packed systems. The viscosity of gelatin sols was studied by Bogue[11] and conformity with Hatschek's formulas could not be obtained. The value *K* which denoted the volume occupied by unit weight of the dispersed gelatin phase was found to rise to a maximum and thereafter decrease upon increasing the gelatin concentration. The increase was explained as due to increasing hydration, and the decrease to competition of the force of surface tension when the film separating the particles becomes very thin.

Swelling and gelation were investigated by Bogue[11] by the addition of increasing amounts of sodium hydroxide and several silicates of sodium, and by Davis, Oakes and Browne[8] by the addition of acids and alkalies. The pH of maximum viscosity was found to be at 3 to 3.5 on the acid side, and at 8 to 9 on the alkaline side. If the dibasic calcium salts are not washed out, however, the rise on the alkaline side is less marked. Davis, *et al.*, even failed to observe any rise at pH greater than 6.0.

Sheppard, *et al.*,[3] have investigated the effects which temperature, concentration, and H-ion concentration have upon the viscosity, jelly consistency, and melting point of gelatins. In this connection they have devised new apparatus for these measurements, which is more scientific than any before described. The jelly strength is measured by exerting a torque upon a cylinder of the jelly and noting the angle of twist at break, and the breaking load. The results obtained have shown a great disparity of uniformity. It seems that the only conclusion which may be drawn thus far is that the several gelatins used differed from each other in such a way that while each produced a typical curve, these bore no exact or parallel relation to each other, and the variations in elasticity were not a simple function of the concentration or the pH.

Theories of Structure

Differences of some importance continue with respect to the structure assumed to exist in gelatin gels and sols. Procter[6] pictures a compound of gelatin with an acid as a coherent mass from which the gelatin cannot diffuse or separate. The net structure is advocated by Robertson,[16] and a honeycomb or sponge structure by Bancroft.[10]

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[*] Numbers in text refer to reference list at end of article.

Bradford[12] affirms the existence of a definitely crystalline structure in gelatin gels, claiming to have obtained gelatin crystals, but Scherrer[19] has found no trace of interference figures of the characteristic space lattice arrangement upon examining gelatin gels by means of the Röntgen photograph.

Fischer[9] continues to urge his hydration theory, in which he regards gelatin gel as a solution of solid hydrated gelatin in gelatin solution, or, if the solvent is limited, a reversal in type of system is indicated and there is produced solid hydrated gelatin holding within itself gelatin solution.

Miss Lloyd[5] has proposed that gelatin gel consists of a solid and a liquid phase, both of which are continuous. Gelation occurs only on the cooling of a sol which contains in solution isoelectric gelatin and gelatin salts in equilibrium with free electrolytes.

A catenary or filamentous structure for both gels and sols was urged by Bogue[20] in 1920 and again in 1922. According to this theory, gelatin sols appear to consist of slightly hydrated molecules united together into short threads resembling streptococci floating about in a dilute gelatin solution. A lengthening of these threads seems to take place as the temperature falls, and at the same time the water-absorbing powder of the gelatin increases. This accounts for the rapid increase in viscosity with drop in temperature. A solid jelly will result only when the relative volume occupied by the swollen molecular threads has become so great that freedom of motion is lost, and the adjacent heavily swollen aggregates cohere. The rigidity seems to depend on the relative amount of free solvent in the interstices of these aggregates, and on the amount of solvent that has been taken up by the gelatin in a hydrated or imbibed condition. The resiliency or elasticity is probably dependent upon the length and number of the catenary threads.

Loeb[1] has recently attempted to explain the differences in the behavior of different proteins upon treatment with water and electrolytes by an *occlusion theory*. The idea is advanced that proteins form true solutions in water which in some instances (*e. g.*, in gelatin sols) contain, side by side with isolated ions and molecules, submicroscopic solid particles capable of occluding water, the quantity of which is determined by an application of the Donnan equilibrium. Those substances which change this equilibrium in the direction of an increased number of solid particles at the expense of the molecularly dispersed particles will produce an increase in viscosity and a decrease in osmotic pressure, while the reverse holds equally true.

CHEMICAL CONSTITUTION

An accurate determination of the amino-acid constitution of proteins has been unknown until very recently. Fischer, Levine and Anders[34] were able to recover only 42.1 per cent of the total nitrogen of gelatin in the amino acids by Fischer's esterification method, and Skraup and von Biehler[35] only 70.7 per cent. By an important modification of Fischer's method, Dakin[21] in 1920 recovered 91.31 per cent of the total nitrogen of gelatin in the amino acids.

By employing the Van Slyke method[36] for the separation of amino-acid groups, Bogue[22] has shown that the gelatins or glues obtained by long action of the water on the stock differ from the material that is first extracted by containing in the solution the hydrolysis products of proteins other than gelatin, as mucin, keratin, elastin, etc. These solutions, as well as the products obtained by the partial hydrolysis of [illegible] also increasing amounts of proteose, peptone, and amino acids. The first extractions are nearly pure solutions of the protein gelatin, but the last extractions contain larger amounts of proteose than protein, and these are derived to an increasing extent from non-collagen (non-gelatin) material.

TECHNOLOGY

The advances in the technology of gelatin and glue have not been so spectacular as in the more theoretical aspects. This is due partly to the disposition of manufacturers to keep secret such improvements as are discovered, and partly to the relatively small number of able colloid chemists who are directly interested in the technological phase of the problem. A number of patents have been taken out upon improved machinery for glue- or gelatin-making. The old method of drying by allowing the liquid to gel in pans, and then cutting the jelly with wires, has been largely replaced by more efficient processes. The Kind-Landesmann machine[37] permits the liquid to run onto a wide endless belt which conveys the liquid through a cool chamber where it gels, and on emerging at the opposite end is transferred to the frames of wire or cloth net for drying. Spray drying has been tried out with some success, and seems to be a highly desirable innovation, as the liquid is rapidly converted into a fine, dry, white powder. Steam-roller drying is used for some products. Improved machinery has also been devised for many other of the manufacturing operations. Continuous extracts for obtaining the gelatin from the stock are of special importance, as much higher grade material may be obtained.

A new system for the evaluation of glues and gelatins has been proposed by Bogue.[38] A method for evaluation that is based upon some fundamental property is needed very sorely, for the methods in common use are both incompetent for accurate differentiation, and the results are purely arbitrary and expressed in terms that mean little or nothing except to the salesman. The proposed system regards the undergraded gelatin content and (for glues) the maximum joint strength obtainable as the most fundamental properties. These are found to be parallel to the viscosity at a temperature near the melting point. The method consists in a measurement of the viscosity at 35° C. of an 18 per cent solution (moisture-free basis) by means of the MacMichael viscosimeter. The results are expressed in centipoises, and the designation of grade referred to this value.

But the forward movement has only begun. We are in an era of chemical progress in industry, and what advance has already been made is but the early glow of that which is later to become the full day.

REFERENCES

1—Jacques Loeb, *J. Gen. Physiol*, **1** (1918–9), 39, 237, 363, 483, 559; **2** (1919–20), 87; **3** (1920–21), 85, 247, 391, 827; **4** (1921–22), 73, 97, 107. "Proteins and the Theory of Colloidal Behavior," New York, **1922**.

2—C. R. Smith, *J. Am. Chem. Soc.*, **41** (1919), 135; **43** (1921), 1350; *J. Ind. Eng. Chem.*, **12** (1920), 878.

3—S. E. Sheppard, S. S. Sweet and F. W. Scott, *J. Ind. Eng. Chem.*, **12** (1920), 1007; S. E. Sheppard and S. S. Sweet, *Ibid.*, **13** (1921), 423; *J. Am. Chem. Soc.*, **43** (1921), 539; S. E. Sheppard and F. A. Elliott, *Ibid.*, **44** (1922), 373; S. E. Sheppard, *Nature*, **107** (1921), 73.

4—A. Kuhn, *Kolloidchem. Beihefte*, **14** (1921), 147.

5—D. J. Lloyd, *Biochem. J.*, **14** (1920), 73.

6—H. R. Procter, *J. Chem. Soc.*, **105** (1919), 315; *Collegium*, **1915**; H. R. Procter and J. A. Wilson, *J. Chem. Soc.*, **109** (1916), 307; J. A. and W. H. Wilson, *J. Am. Chem. Soc.*, **40** (1918), 886.

7—Wo. Pauli, *Trans. Faraday Soc.*, **9** (1913), 54; *Report of the Faraday and Physical Soc.*, **1921**, 14; Wo. Pauli and Hirschfeld, *Biochem. Z.*, **62** (1914), 245.

8—C. E. Davis, E. T. Oakes and H. H. Browne, *J. Am. Chem. Soc.*, **43** (1921), 1526; E. E. Davis and E. T. Oakes, *Ibid.*, **44** (1922), 464.

9—Martin Fischer, "Soaps and Proteins," New York, **1921**.

10—W. D. Bancroft, "Applied Colloid Chemistry," New York, **1921**.

11—R. H. Bogue, *J. Am. Chem. Soc.*, **43** (1921), 1764; *J. Ind. Eng. Chem.*, **14** (1922), 32.

12—S. C. Bradford, *Biochem. J.*, **12** (1918), 382; **14** (1920), 91.

13—E. Hatschek, *Report of Faraday and Physical Soc.*, **1921**, 35.

14—J. O. W. Barratt, *Ibid.*, **1921**, 49.

15—Zsigmondy, *Ibid.*, **1921**, 51.

16—T. B. Robertson, "The Physical Chemistry of the Proteins," **1918**, 325.

17—J. W. McBain and M. E. Laing, *J. Chem. Soc.*, **117** (1920), 1506; J. W. McBain, W. F. Drake, and C. S. Salmon, *Proc. Roy. Soc.*, **98A** (1921), 395.

18—H. N. Holmes, *J. Am. Chem. Soc.*, **42** (1920), 2049.

19—P. Scherrer, *Nachr. Kgl. Ges. Wiss. Göttingen*, **1918**, 96.

20—R. H. Bogue, *Chem. Met. Eng.*, **23** (1920), 61; *J. Am. Chem. Soc.*, **44** (1922), 1313, 1343; *J. Franklin Inst.*, **193** (1922), 795; **194** (1922), 75.

21—H. D. Dakin, *J. Biol. Chem.*, **44** (1920), 524.

22—R. H. Bogue, *Chem. Met. Eng.*, **23** (1920), 105, 154.

23—J. Alexander, *J. Am. Chem. Soc.*, **43** (1921), 434.

24—F. Elliott and S. E. Sheppard, *J. Ind. Eng. Chem.*, **13** (1921), 699.

25—A. W. Thomas, *Ibid.*, **12** (1920), 177; A. W. Thomas and M. W. Kelly, *J. Am. Chem. Soc.*, **44** (1922), 195.

26—F. L. Seymour-Jones, *J. Ind. Eng. Chem.*, **14** (1922), 130.

27—C. E. K. Mees, *J. Franklin Inst.*, **1921**, 631.

28—S. E. Sheppard, Monograph on Gelatin, in press.

29—J. Alexander, A. C. S. Monograph on Gelatin and Glue, in preparation.

30—L. Thiele, "Leim und Gelatine," Leipzig, **1922**.

31—R. H. Bogue, "The Chemistry and Technology of Gelatin and Glue," McGraw-Hill Book Co., New York, **1922**.

32—F. G. Donnan, *Z. Elektrochem.*, **17** (1911), 572; Donnan and Harris, *J. Chem. Soc.*, **99** (1911), 1554; Donnan and Garner, *Ibid.*, **115** (1919), 1313.

33—E. Hatschek, *Kolloid-Z.*, **7** (1910), 301; **8** (1911), 34; *Trans. Faraday Soc.*, **9** (1913), 80.

34—E. Fischer, Levene and Anders, *Z. physiol. Chem.*, **35** (1902), 70.

35—Skraup and von Biehler, *Monatsh.*, **30** (1909), 467.

36—D. D. Van Slyke, *J. Biol. Chem.*, **10** (1911), 15; **22** (1915), 281.

37—M. Kind, U. S. Patent 1,046,307 (1912).

38—R. H. Bogue, *J. Ind. Eng. Chem.*, **14** (1922), 435.

Progress on Emulsions

By Leon W. Parsons

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THIS ARTICLE indicates briefly several main channels through which progress is being made in studying emulsions. Several fairly complete summaries of the literature on emulsions are available, to which the reader is referred for details.[1] With emulsions, the "practice of the art," extensive although incompletely understood, is far ahead of the "science," a condition quite universal in applied colloid chemistry. For discussion, a rough division may be made into theoretical aspects and practical applications, subdividing the latter into, first, the formation of stable emulsions, and, second, the breaking of undesirable emulsions.

Theoretical Aspects

Nature of Phases Used—Frequently, the presence of various impurities in the nonaqueous phase has been unintentionally a major factor in determining the behavior of the resulting emulsions. On account of the complexity of these systems, the writer believes that steady progress will be made only by adopting a more "synthetic" program in studying emulsions, namely, using the purest liquids available for the two phases, and, after determining the characteristics in these supposedly simple systems, building up gradually more and more complex phases, determining the effect of the added substances and comparing the effects with the phenomena encountered in complex commercial systems. Bhatnagar has selected pure British Pharmacopeia paraffin oil for important studies on emulsion stability and in this laboratory Nujol, a highly refined mineral oil, has served very satisfactorily as a nonaqueous phase for studying mineral oil emulsions.

Nature and Function of Emulsifying Agent—This factor has influenced greatly various theories of emulsification. Emulsifying agents are either in true or colloidal solutions or are finely divided solids in suspension. Surface tension does not always play a major role. Briggs mentions several very good emulsifying agents which do not lower the surface tension. Holmes' work on gelatin indicates cases where viscosity rather than surface tension determines the stability. Fischer believes that the emulsifier must be a hydrated or solvated colloid combining with the continuous phase. Bancroft, in correlating earlier theories, states that emulsification is due to a solid or plastic film formed between the two phases by adsorption, the type of emulsion being determined by the wetting of the film by the two liquids, whichever wets the film more becoming the external phase. Data obtained by R. E. Wilson indicate that emulsifying agents form a film possessing the properties of a plastic solid rather than a viscous liquid.

Pickering's early work on finely divided solids as emulsifying agents in which is suggested the idea of relative wetting as a determining factor in influencing the type of emulsion has been continued recently by Briggs, who has shown conclusively the similarity between emulsions obtained with finely divided solids and with so-called soluble emulsifying agents, as soaps.

A new theory is proposed by R. T. A. Mees[2] to explain the emulsifying power of soaps by combining the theory of Harkins and Langmuir which deals with the orientation of soap molecules at interfaces and the previously mentioned hydration theory of Fischer.

Several abnormal effects of emulsifying agents have been observed. In this laboratory, it has been found recently that a solution of sodium oleate, after aging, can produce a water-in-oil (Nujol) emulsion, possibly because of the formation of an acid oleate by hydrolysis, a change in degree of hydration, or the formation of a plastic film in the solution. Similar water-in-oil emulsions are obtained with sodium oleate and stearate when ground in oil and shaken with water, but no such effect was noticed on grinding a polyvalent soap in water and subsequently shaking with oil. Ammonium oleate, a monovalent soap, is said to be capable of producing a water-in-oil emulsion.

In brief, there is urgent need for further work on the soaps and the finely divided solids to correlate their physical and chemical characteristics and their behavior when used as emulsifying agents. More definite data are needed on the quantitative determination of relative wetting, on changes which may accompany abnormal effects, and also on the changes in physical structure of soaps. Photomicrographic methods and the ultramicroscope should prove valuable laboratory tools.

Methods of Preparation—These consist fundamentally in breaking up into droplets what is to be the dispersed phase and then causing the emulsifying agent to go into the inter-

[1] Clayton, *J. Soc. Chem. Ind.*, **38** (1919), 113; Liesegang, *Z. deut. Ol- Fett-Ind.*, **40** (1920), 501; A. A. Thomas, This Journal, **12** (1920), 177; Bancroft, *J. Phys. Chem.*, **16** (1912), 177, 345, 475, 739; **17** (1913), 501; **19** (1915), 275, 513; **20** (1916), 1; Bancroft, "Book on Applied Chemistry," **1921**; "The Physics and Chemistry of Colloids," Report of Faraday Society, October 25, 1920, p. 17; Clayton's book on "Emulsions" being published.

[2] *Chem. Weekblad*, **19** (1922), 82.

[illegible] The [illegible] up [illegible] accomplished mechanically and the emulsifying agent may be added either to the internal phase, may be suspended or dissolved in the continuous phase, or [illegible] at the interface. Briggs has shown that intermittent shaking is considerably more effective than continuous shaking. Clayton believes that shaking is an inferior method of making emulsions, since, as the emulsion becomes more perfect, the smashing action between heavy and light particles decreases, whereas it should increase. He suggests that according to Briggs it would appear that the ideal process of emulsification is one in which the dispersed phase is broken up as much as possible, while the continuous medium is left undisturbed as far as possible; and that continuous shaking might give equally as good results as intermittent, provided the emulsified portions of the mixture are continually removed from the mass so that the energy of shaking is concentrated on the remainder.

Method of Testing Phase Relationships—Both Briggs' drop method and Robertson's color indicator method have been criticized by Bhatnagar; the former, on account of the fact that a single drop may not always represent accurately the emulsion; the latter, on account of possible disturbance to equilibrium by introducing the oil-soluble dye. Bhatnagar has developed an electrical conductivity method for determining the type of emulsion which, it seems, may also be open to criticism because of disturbance of equilibrium. By careful microscopic inspection, aided by a microphotographic attachment, the writer has been able to utilize both the Briggs and the Robertson tests very satisfactorily. Care must be taken, however, to observe closely the internal phase.

Stability—Considerable experimental work is being conducted on the stability of various emulsions. This depends on a number of factors, such as the nature of the emulsifying agent, volume ratio, properties of nonaqueous phase, etc. In emulsions of two pure liquids, the factors affecting stability, such as viscosity, size of particle, difference in specific gravity, and electrical charge, will also influence the stability of emulsions with emulsifying agents, though their effects may not be predominant.

The inversion point evidently marks a region of instability and is of great importance from both a theoretical and a practical standpoint. Clowes and Bhatnagar have both studied this extensively. Similar studies on the effect of different variables on the inversion point have been conducted in this laboratory for Nujol-water systems.

There is a rich field for investigation in studying the action of various electrolytes on the properties of emulsions. Bhatnagar has extended the early work by Donnan, Ellis, Lewis, and Hatschek and has pointed out the resemblance between neutral oil emulsions and suspension colloids. He records a parallelism between the reversal of phases in emulsions and the precipitation of colloid sols in suspensions, and indicates the possibility of clearing up the mysteries of coagulation and of developing a rational theory of colloidal solutions and emulsification.

Practical Applications

[illegible] Emulsions—Many liquid emulsions [illegible]. The U. S. Bureau of Entomology is studying oil emulsions for contact insecticides and is obtaining interesting results with a nicotine oleate emulsion. The [illegible] greatly. The [illegible] being investigated by several oil companies, the chief difficulty being in the selection of the most suitable oil-soluble colloids. [illegible] light fuel for use in [illegible].

Many [illegible] emulsions, are of great commercial importance. Clayton has studied carefully the production of margarine, one of the most complex solid emulsions. By different mechanical treatments with the same material, either type of emulsion may be obtained and the problems in margarine manufacture offer an extremely fertile field for research. The emulsion chemistry of household products, such as mayonnaise, has undergone considerable development. A systematic study of lubricating greases (water-in-oil emulsions) is greatly needed. Various polishes and creams, including toilet preparations, offer great opportunities for development to the colloid chemist. Asphalt emulsions are finding extended use for paving purposes and for application to paper pulp in forming water-resistant stock. Emulsification of mineral oils in the cooking of rags for paper stock has been studied recently.

Some other systems involving emulsions which are being studied are: ready mixed paints; emulsified fats for leather; artificial leather; emulsions of japan in water; soap emulsions of fat solvents; rubber latex; and biological phenomena.

Breaking of the Emulsions—A beginning is just being made to study systematically the breaking of undesirable commercial emulsions, such as those encountered in refining wool fat and particularly in the petroleum industry. At the recent emulsification symposium of the Petroleum Section[3] the general nature of the problems involved was indicated. The systems are extremely complex and illustrate clearly the aforementioned need for more careful synthetic studies. The Bureau of Mines at its Oklahoma Station is starting an investigation of oil field emulsions. This laboratory is also conducting a fundamental investigation of commercial petroleum emulsions. The American Petroleum Institute has outlined a program for studying this problem.

In conclusion, it may be noted that there is great activity along both theoretical and practical lines on emulsion research. Considerable information is necessarily kept secret by various companies, but there is a keen desire to obtain accurate scientific data on emulsions and to apply such data to their particular problems. The need for coöperative research between universities and commercial laboratories is great and, with the rapid advances which have been made in colloidal chemistry during the past ten years, the results of such coöperative research should be extremely valuable.

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[3] This Journal, 13 (1921), 1008.

Inventions by British Government Workers

A committee of representatives of British governmental departments and British scientific men has recently recommended a comprehensive scheme of dealing with inventions by government workers or by individuals aided or maintained from public funds. The committee recommends the organization of an interdepartmental patents board. Pending a decision in each case by this board, all rights in inventions made by government employees shall belong to the government. If the inventor can satisfy the board that he derived no assistance from the nature of his employment in making the invention, he shall be entitled to all rights therein. The question of whether the inventor is entitled to any reward in addition to the enjoyment of commercial rights shall be decided by the board. Where the rights in an invention capable of commercial exploitation belong to the government, the invention shall be exploited commercially for the benefit of the government. A system of awards and merits for the inventor is proposed, which should be passed upon by an awards committee, to be organized within the proposed patents board. These are not intended as substitutes for commercial profits, but as a recognition of merit and as an incentive to government workers.

Many people were overcome and $1,000,000 damage was done by a fire in the storage warehouse of the Manufacturers' Transit Co., New York City, July 18. Explosions of magnesium powder used largely in flashlights, were responsible for the blaze.

Vegetable Glue

By C. K. Reiman

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VEGETABLE glue may be defined as a homogeneous mixture of starch, water, and a solvent for amylocellulose such as caustic soda, having the appearance and many of the adhesive properties of animal glue. Cassava (tapioca) starch generally forms the basis of this material. The water content varies from 2 to 4 times the weight of the starch and the caustic is generally about 5 per cent and may vary between 2 and 12 per cent of the weight of the starch. The vegetable glues find their widest use in the veneering industry. They produce a joint as strong as animal glue. They are mixed hot but used cold and they will keep ready for use without deterioration for weeks. They do not have the waterproof qualities of casein, being about the same in this respect as the animal glues. Their chief disadvantage is the tendency of some of these glues to stain certain woods.

Clarence K. Reiman

Patent Controversy

The earliest reference to such a material concerns apparatin, a product patented nearly half a century ago (1874) by Gerard, a Frenchman. This material consisted of what is generally called a solution of starch in caustic and water. It was described as having excellent adhesive properties, and as being useful in the field of textile sizing and as an adhesive for various purposes.

Two others of the many patents dealing with such products deserve attention. In 1897 a patent was granted to Higgins describing an adhesive prepared from a starch that had been partially hydrolyzed by treatment with dilute acids. The various stages through which the starch progressed during this treatment were accurately described. The fact was pointed out that increased strength of joint was obtained by so treating the starch. In 1906 Gerson and Sasche were granted a patent in Germany covering a process for the partial hydrolysis of starch by means of an alkaline oxidizing agent, and the starch base so produced.

Since that time a large patent literature has been produced in various countries on this subject. To-day there are a number of important suits in progress in which the courts are endeavoring to determine to whom should be given the credit for the actual inventions declared in these many patents.

The reason for the court activity at the present time over these old patents is because of the considerable importance which vegetable glues have acquired in the woodworking industry. With the enormous growth in the production of plywood panels and veneered furniture, and with the generally rising price of animal glue the need of a cheaper adhesive for this purpose became more and more urgent.

The first vegetable glues made for this use consisted of raw starch, either potato or cassava, cooked with 8 or 10 per cent of caustic and 3 to 5 parts of water. A 3-ply or a 5-ply panel glued with this type of adhesive contained so much water that drying was difficult, and a large percentage of failures occurred owing to opening up of the glue joints. Animal glue used for this purpose was generally mixed with 2 parts of water. When the raw starch was used with 2 parts of water the resulting glue was altogether too thick to spread, either by hand or by the mechanical spreaders then used with animal glue. It was after this point had been appreciated that the various parties interested in introducing vegetable glue into the veneering field turned for assistance to the almost forgotten patents concerning the partial hydrolysis of starch. When a starch base was used, which had been previously hydrolyzed according to the methods of Higgins or Gerson and Sasche, a glue could be prepared with caustic using the same amount of water that was used with animal glue.

In 1912 the first of a series of patents in the vegetable glue field was granted to Perkins. This patent covered a large number of claims; some of which had to do with the processing of the starch by methods practically identical with those of the earlier patents; some of which dealt with the solution of the starch in caustic with three or less parts of water, the patentability of which has been widely questioned; and other claims which covered the combination of these two steps. In the only case that has come to the Court of Appeals the Perkins patent has been upheld in part, that is, it was declared that neither step alone was patentable but that a combination of the two was.

At the present time there are several large manufacturers of these vegetable glues supplying the plywood and veneering industries. Many of the users of these glues are to-day defendants in suits brought by Perkins. A number of these glue manufacturers and certain organizations composed of the users of these glues have banded together in the defense of these suits. As the outcome is uncertain, both sides are interested in forcing a decision in the near future which will at least serve to clear the air of the large amount of dust at present obscuring activities in these fields.

Current Practice

It is interesting to note that to-day current practice is drifting away from the type of glue described in the Perkins patents. Several of the glue manufacturers have discovered that it is unnecessary to process their starch with dilute acid solutions or alkaline oxidizing agents in order to make a workable glue when mixed with caustic and 2 or $2^1/_2$ parts of water. In practice, if the raw starch is properly cooked with the caustic a workable glue will result. In fact, some of the important developments of recent date have been in the opposite direction from that indicated by Perkins. It has been found possible to so adjust the gel properties of the starch by the addition of certain colloidal materials, that a product as strong as animal glue is obtained when 4 parts or more of water are added to the starch and caustic. It is obvious that greater economy is obtainable when a glue kettle containing 500 lbs. of mixed glue is prepared with 100 lbs. of starch than when 200 lbs. are required. In fact, the spread obtainable with the glues of the older type containing 2 or 2$^1/_2$ parts of water averages between 45 and 55 sq. ft. of glue line per lb. of dry glue. With the 4 : 1 glues to which certain colloidal materials have been added this spread is easily doubled. Thus, it becomes apparent that the amount of water to be dried from a panel glued with a 4 : 1 glue varies but little with that to be dried from one glued with a 2 or 2$^1/_4$: 1 glue, since with the former the same amount of starch spreads twice as many panels.

EXTENT OF INDUSTRY

The extent of the vegetable glue industry is apparent when it is appreciated that there is an annual market in this field for 20 or 30 million lbs. of starch in this country alone. There are about 1000 concerns using vegetable glues in the manufacture of standard panels, box-shooks, and furniture. There are perhaps a dozen concerns producing these various vegetable glues. The price to the consumer of these vegetable glues is between 6 and 9 cents per lb. A fair price for animal glues for the same purpose to-day is between 13 and 20 cents, and in the past has been even higher. Thus, there is a saving of at least one-half the glue bill when ordinary 2 : 1 vegetable glue is substituted for animal glue and this figure can be reduced further by employing the 4 : 1 glues recently developed.

It should be pointed out there are many varieties and grades of starch, and that not all of them are of equal value in producing a vegetable glue. Moreover, there is a wide variation in most of these grades of raw starch, which makes it a precarious venture for a plywood manufacturer to buy raw starch on the open market and turn this material into a veneer glue. Unless he has a chemist familiar with starches and vegetable glues and capable of maintaining a uniform product, the few cents per pound saved on materials cost will be far overbalanced by the losses from poorly glued stock.

Colloid Chemistry

By Jerome Alexander

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THE GROWING realization of the importance of colloid chemistry and its practical applications is evidenced by the fact that whereas the Decennial Index of *Chemical Abstracts* (1907-1916) contains a little over 12 columns of titles indexed directly under colloids, the 1921 index alone contains over 3 columns. In both cases no note has been taken of a large number of titles of papers dealing with colloid-chemical questions, but indexed under a wide variety of other heads.

The *Kolloid Zeitschrift*, which appeared initially in 1906, is now in its 30th volume, and 14 volumes of monographs have been issued in *Kolloidchemische Beihefte*. Since its organization the National Research Council has had its Committee on Colloids, and the British Association for the Advancement of Science has considered the subject of such importance, that since 1917 it has issued three "Reports on Colloid Chemistry and Its General and Industrial Applications." Each report contains a series of separate papers; a fourth report is in press, and a fifth is in preparation. A few years ago the Chemical Society of London and the Faraday Society held a special joint symposium on colloid chemistry which was attended by quite a number of prominent continental chemists, and though the papers read were published in several journals, they were deemed of such importance that they were printed separately, together with [illegible] work.

Many universities and colleges here and abroad are giving separate courses in colloid chemistry, and no course in theoretical or technical chemistry is complete without giving it due consideration. Analysts, biologists, and physicians must [illegible] it. In [illegible] every branch of chemistry and technology, workers of unquestioned reputation and ability are producing striking results. Why is it, then, that there are still some who shrink from recognizing colloid chemistry as a [illegible] chemical and physical [illegible] chemical [illegible] be explained upon the basis of "simple chemical principles?"

Just criticism has been leveled at some who fail to give due weight to purely chemical considerations, or who think that a problem may be dismissed with the mere statement that it is "colloidal." But the main cause of the tendency referred to is an attempt to stretch the original and long-established meaning of the term "chemical" to cover all cases where attractive forces result in combination. Thus S. H. C. Briggs[1] goes so far as to consider as "chemical" the forces which hold atomic kernels and electrons together to form elements. If, with Langmuir, we call all residual electronic forces "chemical," then adsorption compounds are chemical compounds. Atoms or molecules without a residual field of force would form a perfect gas, but even helium does not meet this criterion. Elemental atoms and all molecules are anisotropic or polar, and after the satisfaction of what have been heretofore regarded as the normal chemical valences, there remain powerful residual or stray fields of electronic force which are responsible for what we ordinarily term the physical properties of the substance—its hardness, melting point, boiling point, solubility, viscosity, etc.

Champlain Studios, N. Y.
JEROME ALEXANDER

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[1] *Phil. Mag.*, **42** (1921), 448.

Much difficulty would be avoided if we adopt the classification suggested by P. E. Wells:

1—Electronic forces—those which bind electrons together into atoms.

2—Atomic forces—those which bind atoms together into molecules.

3—Molecular forces—those which bind molecules together into masses.

4—Molar forces—those which affect masses, *i. e.*, gravitation.

There is no sharp demarcation between 2 and 3, and the forces involved in colloid phenomena bridge the gap.[2] So after the novice is taught to distinguish between physical mixtures and chemical compounds, he must gradually learn that no sharp distinction exists.

Without in any way attempting to give a complete or even a critical selection from the wide field, there are here briefly mentioned a few colloid subjects of theoretical interest, followed by a number of instances where recent developments in colloid chemistry have been applied to technical problems:

Theoretical

1—It seems probable that changes in sensitive bio-colloids constitute one important mechanism whereby evolution proceeds.

2—It has been shown that adsorbed ions are necessary to the formation of stable colloidal solutions and jellies.

3—Nephelometers have been developed and applied to many quantitative determinations.

4—With the MacMichael viscosimeter the viscosity of colloids may now be expressed in absolute or c. g. s. units.

5—The size of colloidal particles has been checked with the aid of an oscillating electric field.

6—Much work has been done on fogs, smokes, and adsorbents.

7—Much work has been done on catalysis, its acceleration and inhibition.

8—M. H. Fischer and Wo. Ostwald, among others, have shown the importance of the state of swelling, or solvation in colloids.

9—After showing the importance of H-ion concentration in protein solutions, J. Loeb applied the Donnan theory of membrane equilibria as developed by Procter and Wilson, and worked out a mathematical and quantitative theory of the colloidal behavior of proteins.

10—McBain has developed the idea of colloidal electrolytes, *i. e.*, salts in which one of the ions is replaced by a heavily charged hydrated ionic micelle (a colloidal particle of great conductivity).

11—Many biological reactions have been explained on the basis of colloid chemistry,—*i. e.*, clotting of blood, coagulation of milk, Wassermann reaction, anaphylaxis, etc.

12—Ultrafiltration and ultracentrifugation have been developed.

13—Ultramicroscopy has made rapid strides.

14—Swelling and shrinking of colloids have received wide attention from an experimental and from a theoretical standpoint.

15—The making and breaking of emulsions as well as their reversal of phase have been much studied.

16—Many applications of colloid chemistry to chemical analysis have been noted.

Technical Applications

1. Flotation—Over 60,000,000 tons of ore are treated annually. Adsorption, surface tension, and flocculation are important factors here, and because of the great commercial interests involved, much work has been done on the theoretical and practical sides of flotation problems.

2. Colloidal Adsorbents (silica-gel, specially prepared carbons, fuller's earth)—The importance of proper carbon for gas masks was proved during the war. Patrick's silica-gel is largely used to recover casinghead gasoline, and petroleum distillates are purified by various adsorbents. Zerban reports that impurities in cane-sugar juice are largely colloidal and mainly removable by adsorption,—*i. e.*, with 0.5 per cent Filtercel and 1 per cent Norit.

3. Colloid Mills—These are essentially high-speed disintegrators arranged for wet grinding. A protective colloid is usually added to the water or other fluid used, to prevent re-aggregation of colloidal particles originally formed. The mill is said to find application in the following industries: soap, viscose, cellulose, oil, rubber, sugar, and glue. Products of special properties are without doubt produced, but until definite information is had as to output, cost of power and repairs, judgment as to the commercial status of the mill must be suspended.

4. Ultracentrifuges (and ultrafilters) have been applied to the clarification of many fluids,—*i. e.*, varnishes, wool-scouring liquors (with recovery of wool grease), gelatin.

5. Water-Purification and Sewage Disposal—The *Journal of the American Water Works Association* shows many extensions in this field. New sand filters do not function properly until a bacterial gel or slime forms on their surfaces. The same applies to sewage filters.

6. Tanning—Much valuable work has been done by H. R. Procter and J. A. Wilson, who have applied Donnan's theory of membrane equilibria, which for some time lay buried in the *Zeitschrift für Elektrochem.*

7. Lubrication—W. B. Hardy showed that powerful adsorption at the interfaces involved is an essential in lubrication. Southcombe and Wells patented the addition of a small amount of free fatty acid (about 1 per cent) to petroleum oils. This lowers the interfacial tension between oil and metal. The surface tension between oil and graphite is less than between oil and metal; hence graphitizing aids lubrication.

8. Colloidal Fuel—This consists of finely powdered coal, tar, etc., dispersed in fuel oil with the aid of a protector (usually a lime soap). Most of the dispersed material is far above colloidal dimensions, so the fuel has a "life" limit that may extend to months, after which it may be "revivified" by agitation. It should economize fuel oil and use up culm and other wastes.

9. Metallurgy—Properties of metals and alloys are dependent upon fineness of grain, and this may be partially within the colloidal zone. Scherer showed that even amicroscopic particles of colloidal gold consist of crystals, but that with colloidal silica and stannic acid crystalline and haphazard or amorphous groups of molecules may coexist.

10. Petroleum—The viscosity of oils depends upon their previous history, probably because of variations in the degree of dispersion of waxy bodies present. The breaking of emulsions in refining and their formation in lubrication are colloidal problems.

11. Clay—The use of deflocculators in purifying and casting clays has been largely developed.

12. Agriculture—Colloid problems in soils and fertilizers are being widely investigated. A small amount of "ultra-clay" produces a powerful effect on a soil.

13. Insecticides,—*i. e.*, lead arsenate, are more efficient and stick better when in colloidal state. Minute quantities are sufficient to kill insects, and it is wasteful to supply more than the necessary dose.

14. "Firefoam," used in blanketing fires, is a carbon dioxide froth made by mixing solutions of alum and sodium bicarbonate. A protective colloid, such as glue, dextrin, or saponin, is used to stabilize the finely dispersed foam.

15. Rubber—The importance of the state of subdivision of "fillers" is recognized. Much work has been done on vulcanization, and on the coagulation of latex. Glue is now worked into rubber tires on a large scale, and is said to improve their life.

16. Baking and Bread-Making—The swelling and viscosity of glutens are being investigated, also the prevention of "staling" by milk, fat, etc. The effect of traces of salts on flour is important.

17. Varnishes, Paints and Pigments—Work has been done on thickened oils (linseed and china wood oil), resins and synthetic resins (bakelite), and varnishes. The degree of subdivision of pigments in paints, and their maintenance in dispersion and suspension are important factors in paints.

18. Milk and Milk Products—Ice cream is improved, stabilized, and made more digestible by protective colloids (gelatin, eggs, etc.). Homogenized milk and cream having increased viscosity are largely used, and artificial milks are made. Protective colloids are used in preparing margarines. Little work has been published in regard to cheese.

Besides translations and new editions, increasing numbers of books are appearing originally in English. Laboratory manuals have been issued by E. Hatschek and by H. N. Holmes. In 1921 W. D. Bancroft published in This Journal a list of 200 research problems in colloids, which list was issued separately by the National Research Council.

In looking up indexes for references, it must be borne in mind that many papers and books of interest to the colloid chemist are not indexed under "colloid." Such headings as gel, sol, hydrosol, jelly, emulsion, coagulation, etc., should be consulted, and many papers, especially those listed in *Chemical Abstracts* under General and Physical Chemistry, and Biological Chemistry, contain colloid chemical work. Thus W. E. S. Turner's book on "Molecular Association" (p. 99) has the following pertinent statement:

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[2] In fact many, among them Faraday, have expressed the view that there is only one ultimate kind of force.

> **The formula of a substance shall be recognized as a function of the physical conditions under which it exists, so that the formula for elements is X_n, for compounds $(XY)_n$, where n is to be specified according to the conditions. Although we are far from realizing how n varies for most substances, the adoption of such formulas would bring home clearly the fact that both the physical and the chemical behavior of the substance may be closely dependent on the value of n.**

The Chemistry of Intermediates

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THE PERIOD under review is particularly marked by the successful application of sound physicochemical principles to the solution of the complex problems involved in the manufacture of organic compounds. More than ever before, it has been demonstrated that physics and chemistry are indissolubly linked and that in this union is great potential power for use in the service of humanity. Much of the progress made in the chemistry of intermediates during the past few years has been due to the combined efforts of organic and physical chemists. The catalyst has been the key to unlock many molecules and thus permit reactions not otherwise realizable. Our knowledge of surface phenomena is rapidly leading to a better understanding of the mechanism of chemical reactions.

In one other respect the past few years in the chemistry of intermediates have been noteworthy, that is, in the ever-increasing evidence of the interdependence of dye intermediates and pharmaceutical products. Salicylic acid has given us an excellent nontoxic local anesthetic—salicyl alcohol, and some complex carbamide of the naphthalene series involving H acid is probably the future remedy for sleeping sickness. Although the constitution of "Bayer 205"[1] is not disclosed, it is thought to be one of the several carbamides or closely related substances on which so much research activity centered in Germany during the years 1914–1916.

Progress has been diversified. In a few instances the results have led to the production and utilization of new compounds, while in the majority of cases the achievements have not been epoch-making but rather the necessary improvements to make already existing processes adaptable to modern economic conditions or the development of new processes for old products.

Carboxylic Acids

Both catalytic and electrolytic processes have been developed for the manufacture of carboxylic acids. At the present time the catalytic processes appear to be more economical and practical. Acetic acid[2] is obtained by the catalytic oxidation of acetaldehyde and benzoic acid[3] by both catalytic and electrolytic oxidation of toluene. Many substances have been tried as catalysts in the air oxidation of toluene and naphthalene, and vanadium pentoxide has been chosen, in most cases, as the most suitable for the purpose. It has been shown that a high-grade benzoic acid can be obtained by fusing benzene sodium sulfonate with sodium cyanide.[4] The practical application of this process is, however, questionable. Benzoic acid has also been made by a modification of the Friedel and Crafts reaction[5]—passing phosgene into benzene and carbon bisulfide at a low temperature, then adding aluminium chloride and subsequently hydrolyzing to benzoic acid and recovering the carbon bisulfide. If carbon bisulfide is not used, benzophenone is the main product of the reaction. The benzophenone is converted into benzoic acid by fusing with caustic. This process for benzoic acid is interesting but it does not seem capable of ultimately competing with the catalytic process. It should be of great importance as a process for the manufacture of benzophenone when this product is required as a dye intermediate.

Intensive and well-executed researches on the catalytic air oxidation of benzene and naphthalene have resulted in processes for the manufacture of maleic[6] and fumaric acids from benzene and phthalic acid[7] from naphthalene. It is difficult at this time to correctly evaluate the contribution that these discoveries will make to the economic development of our time, but it is safe to say that they appear to be the most important contribution to the progress of the synthetic organic chemical industry made during this period. With cheap maleic and fumaric acids available new industries will arise. Fumaric acid may yet be the initial raw material for the synthesis of indigo.[8] Cheap phthalic anhydride makes possible synthetic anthraquinone, and this means unhampered progress in the development of the anthraquinone dyes, particularly indanthrene and other vat dyes. Phthalic anhydride will become of increasing importance in the manufacture of intermediates. A new intermediate[9] for azo dyes is prepared by combining phthalic anhydride with 1,7-aminonaphthol.

Sulfonic Acids

Sulfonation has received considerable attention of late. A continuous process,[10] introducing the sulfuric acid and the hydrocarbon through atomizers into the upper portion of a steam-jacketed tower provided with a condenser, permits the reacting mass to flow down the tower over baffled plates, thus completing the reaction. The product is drawn off at the bottom of the tower and any condensed hydrocarbon returned to the charging apparatus. It has been found that certain catalysts enhance sulfonation and in some cases affect the orientation of the sulfonic group.[11] Benzoic acid, when sulfonated in the presence of a small quantity of iodine, gives the *o*-sulfonic acid.[12] A small quantity of anhydrous sodium sulfate and vanadium pentoxide used as a catalyst in the sulfonation of benzene doubles the amount of benzene sulfonated per minute.[13] By the use of a small quantity of iodine[14] as a catalyst certain sulfonations are made possible with weaker sulfuric acid than would otherwise be required. The time of sulfonation is also shortened. This catalyst is particularly suitable for sulfonations of benzene compounds containing substituents such as OH, NH_2, COOH or halogen, but works with difficulty or not at all with compounds of the benzene series containing SO_3H or NO_2 groups. Other catalysts[15] have been studied and in certain cases found to have marked influence on both the quality and the yield of the sulfonated product.

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[1] [illegible] for 1921," *Chem.* [illegible] **18** [illegible]

[2] [illegible]

[3] [illegible] **40** [illegible]

[4] *Chem. Met. Eng.*, **24** (1921), 638, 697.

[5] This Journal, **14** (1922), 406.

[6] U. S. Patents 1,318,632, 1,318,633, 1,377,534.

[7] This Journal, **14** (1922), 120; Brit. Patents 164,785, 145,071.

[8] *J. Am. Chem. Soc.*, **44** (1922), 216.

[9] Brit. Patent 145,057.

[10] Brit. Patent 147,967.

Certain definite progress has been made in bringing about difficult sulfonations. The problem of finding a satisfactory method for the preparation of chlorobenzene-disulfonic acid has been solved by sulfonating *p*-chlorobenzenesulfonyl chloride[16] with monohydrate at 160° to 180° C. The yield is said to be quantitative. The resulting product is 4-chlorobenzene-1,3-disulfonic acid. Again it has been shown definitely that the product obtained by the sulfonation of metanilic acid is the 3,6-disulfonic acid[17] of aniline. Sulfanilic acid when heated with a mixture of sulfuric acid and phosphoric oxide at 180° C. for eight hours gives aniline-2,4,6-trisulfonic acid. The yield is poor and the process needs further refinement.[18]

ALDEHYDES

Considerable progress has been made in the preparation of aldehydes on an industrial scale. Acetaldehyde has been made in large quantities from acetylene. Where cheap power is available this should be a practical process for the manufacture of acetaldehyde and its derivatives, particularly acetic acid. Cheap acetic acid is indispensable to the development of the cellulose acetate industry. Benzaldehyde is obtained by catalytic air oxidation[19] of toluene and salicylaldehyde[20] by oxidizing *o*-cresol in the vapor phase with air or a suitable gas containing oxygen in the presence of a metallic oxide which serves as a catalyst. Electrolytic processes have also been developed for benzaldehyde but it is still uncertain whether they are practical. A very interesting catalytic process for hydroxyaldehydes consists in treating phenol or derivatives of phenol with formaldehyde in the presence of nitroso compounds. Vanillin is prepared by treating guaiacol[21] with formaldehyde in the presence of *p*-nitrosodimethylaniline.

AMINES

The progress in catalytic reduction of cyclic nitro compounds to the corresponding amines has been slow and uncertain. Many processes have been developed but it appears that they are still in an experimental stage. An almost quantitative yield of aniline[22] is claimed to be obtained by passing a mixture of nitrobenzene vapor and hydrogen or water gas or an alcohol capable of giving hydrogen on dehydrogenation over heated copper oxide. Several catalysts have been studied. Some are effective in the liquid phase and others in the vapor phase. Certain compounds of the type $R{-}CH{=}NR$[23] are reduced to secondary amines by passing hydrogen in the liquid containing a suspension of finely divided nickel. The researches on catalytic reduction continue with unrelenting vigor.

Some progress has also been reported in the reduction of certain substituted nitro compounds with different reducing agents. *p*-Nitrophenol, 2,4-dinitrophenol, and the *o*- and *p*-nitrobenzoic acids have been reduced to the corresponding amines by iron and sulfurous acid.[24] Certain other nitro compounds have been reduced to the corresponding hydroxylamines or amines in an aqueous emulsion with alkali sulfides. Nitrobenzene gives by this method a yield of 72 to 74 per cent of practically pure crystalline β-phenylhydroxylamine. Mononitroaniline and *p*-nitroaniline are reduced to the corresponding diamines.[25]

The catalytic alkylation of amines has received some attention. A mixture of monomethylaniline and dimethylaniline has been obtained by passing a mixture of aniline and methanol over aluminium oxide or silica gel. Methylxylidines and naphthylamines have also been prepared by similar processes, that is, by passing a mixture of alcohol and amine vapors over alumina at 360° to 380° C.[26] The butylanilines have been prepared and are now available as intermediates. Likewise, N-methylvinylaniline[27] has been prepared and studied. The unsaturated group is hydrolyzed later to acetaldehyde. A catalytic process for diethylaniline[28] has been described, which consists of heating aniline hydrochloride, ethyl alcohol and a mixture of sodium bromide, cupric chloride, and calcium chloride for several hours in an autoclave. Alkyl-*m*-phenylenediamines[29] are prepared by heating primary or secondary alkylamines or their salts with resorcinol. The reaction appears to be accelerated by sulfurous acid.

Improved processes have appeared for the preparation of neutral alkyl esters of sulfuric acid to be used as alkylating agents. Diethyl sulfate[30] is made by passing an excess of ethylene or mixtures of ethylene and an inert gas into monohydrate or into a sulfuric acid solution of ethyl hydrogen sulfate at about 75° C., and subsequently either extracting the diethyl sulfate with ligroin or benzene or using the reaction product directly for alkylation. A process has also been patented to make dialkyl sulfates by treating acyclic alcohols with SO_3 in the presence of dehydrating agents such as phosphorus pentoxide, anhydrous sodium sulfate or anhydrous copper sulfate.[31]

Certain new amino compounds have been proposed as intermediates. *m*-4-Xylidine-5-sulfonic acid[32] and 6-nitro-*m*-4-xylidine[33] give, when diazotized and coupled with certain phenols, naphthols, and their derivatives, azo dyes and lakes superior in fastness and brilliancy in hue to similar dyes made from xylidine. Cyclic nitroamines[34] are obtained by boiling chloronitrocylic compounds with ammonium acetate. 2,4-Dinitroaniline is obtained by saturating acetic acid of 80 to 90 per cent strength with dry ammonia gas and then adding slowly 1,2,4-chlorodinitrobenzene, maintaining the temperature of the reaction between 124° and 130° C. Ammonia is passed into the reacting mixture during the reaction to replenish the ammonium acetate as fast as it is used up. Methyl-β-naphthylamine-6-sulfonic acid[35] is produced by heating a mixture of Schaeffer salt, methylamine hydrochloride, and caustic soda solution in a rotating autoclave at 180° to 200° C. for six to seven hours. A yield of 72 to 74 per cent of the sodium salt of the acid is obtained. This promises to be an important initial product for the preparation of the N-substituted derivatives of β-naphthylamine. Acyldiaminodiarylsulfones[36] appear to be useful intermediates. They are prepared by the acetylation of diaminodiarylsulfones synthesized from the corresponding chlorodinitro compounds and alkylsulfinic acids. Methyl-β-naphthylamine has been condensed with p-toluenesulfonyl chloride to give the corresponding toluene-p-sulfonylmethyl-β-naphthylamine,[37] which serves as the initial product for the preparation of a new group of intermediates. N-Arylthiomorpholines[38] are obtained by condensing primary cyclic amines having a free ortho position to the NH_2 group with β,β'-dichlorodiethylsulfide. They are proposed as dye intermediates. When β-naphthylamine is sulfonated with 94 per cent sulfuric acid a mixture of 35 per cent of the 8-sulfonic acid and 65 per cent of the 5-sulfonic acid, together with small quantities of the six and seven isomers, is obtained.[39] The mixture of isomeric sulfonic acids is converted into the corresponding sodium salts and these are separated by crystallizing them from sulfuric acid solution.

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[11] *J. Chem. Soc.*, **117** (1920), 1405.

[12] *Ibid.*, **117** (1920), 1405.

[13] THIS JOURNAL, **12** (1920), 968.

[14] *J. Soc. Chem. Ind.*, **40** (1921), 40A, 715A

[15] Private communication.

[16] Ger. Patent 260,563.

[17] *Rec. trav. chim.*, **39** (1920), 499.

[18] *Ibid.*, **39** (1920), 194.

[19] Brit. Patent 165,076.

[20] U. S. Patent 1,380,277.

[21] Brit. Patent 164,715.

[22] *Bull. soc. chim.*, **29** (1921), 217; Brit. Patent 166,283.

[23] *Compt. rend.*, **172** (1921), 280; *Bull soc. chim.*, **29** (1921), 106.

[24] Brit. Patent 165,838.

[25] *J. Chem. Soc.*, **119** (1921), 765.

[26] *Compt. rend.*, **171** (1920), 1154.

[27] *Ber.*, **52** (1919), 2261.

[28] THIS JOURNAL, **12** (1920), 636.

[29] Brit. Patent, 168,689.

[30] Brit. Patent 157,578; *J. Soc. Chem. Ind.*, **40** (1921), 195A.

[31] Brit. Patent 143,260.

[32] Brit. Patent 164,053.

[33] *J. Chem. Soc.*, **119** (1921), 717.

ANTHRAQUINONE AND ITS DERIVATIVES

Particular activity has centered on anthraquinone and its derivatives. Anthracene is now satisfactorily oxidized to anthraquinone by catalytic[40] and electrolytic[41] methods. Synthetic anthraquinone is a reality and the future of the anthraquinone dyes is assured.

Many new derivatives of anthraquinone have been prepared. β-aminoanthraquinone is chlorinated to 3-chloro-2-aminoanthraquinone[42] in an inert organic solvent and 1-hydroxyanthraquinone dissolved in nitrobenzene is chlorinated in the presence of a small quantity of iodine and a sufficient amount of solid sodium carbonate to neutralize liberated hydrochloric acid to 1-chloro-4-hydroxyanthraquinone.[43] It has been shown that the dibromoanthraquinone used by Graeber and Libermann in the synthesis of alizarin was not the 1,2-dibromo product as they thought, but the 2,3-isomer.[44] β-Halogen derivatives of anthraquinone[45] result when α-halogen anthraquinones are heated with sulfuric acid to 200° C. This is an interesting case of intramolecular isomerization and necessitates research to establish the mechanism by which it and similar reactions come about. Alkylaminoanthraquinones[46] are produced by the action of alkyl sulfates on aminoanthraquinone in the presence of a mild alkali and in an inert high-boiling solvent like nitrobenzene. Arylaminoanthraquinones[47] are formed by treating an aminoanthraquinone containing one or more NH_2 groups with metal amides and in the presence of primary cyclic amines such as aniline or its homologs.

BENZOPHENONE

In view of the fact that benzophenone has been prepared from benzene[48] and that such a process should give a relatively cheap product it is important to know that very vivid scarlet dyes, fast to light, fulling and washing are produced from 4,4'-diaminobenzophenone[49] by tetrazotizing and coupling the resulting tetrazotized product with β-naphthols and β-naphtholsulfonic acids.

PARA-CYMENE

A determined effort is being made to utilize p-cymene—a waste product from the sulfite-cellulose industry. It is nitrated and reduced in alkaline medium to hydrazocymene,[50] which is then rearranged to the corresponding 3,3'-dimethyl-6,6'-diisopropylbenzidine. 5-Nitro-2-amino-1-methyl-4-isopropylbenzene, 5-amino-2-acetylamino-1-methyl-4-isopropylbenzene, and 2,6-diamino-1-methyl-4-isopropylbenzene have been prepared from cymene and proposed for intermediates for azo dyes.[51] Aminocymene has been proposed as an intermediate for azo, sulfur, and indigoid dyes.[52]

HYDRAZINES

Certain cyclic hydrazines have been prepared and converted into the corresponding pyrazolones. The process for p-nitrophenylhydrazine[53] has been improved by the substitution of ammonium sulfite for sodium sulfite in the reduction. By condensing phenylhydrazine-m-sulfonic acid[54] with dioxytartaric acid a pyrazolone is obtained which dyes wool and silk a yellower hue than ordinary tartrazine. The 1,4- and 1,5-naphthylhydrazinesulfonic acids[55] give pyrazolones which dye wool and silk red and brownish red colors.

HYDRONAPHTHALENES

Marked progress has been made recently in the production and utilization of hydrogenated naphthalene.[56] It is found to be an excellent solvent particularly useful in the purification of naphthalene[57] when a very pure product is required. Several derivatives of di- and tetrahydronaphthalenes have been prepared and used as intermediates for azo dyes.

It is not possible at the present time to say just what advantages the hydrogenated derivatives of naphthalene possess as intermediates. The difficulties in nitrating the hydrogenated naphthalenes appear to have been overcome and both nitro[58] and amino[59] compounds are now made. Tetrahydro-β-naphthol,[60] difficult to obtain by hydrogenation of β-naphthol, is now obtained by sulfonating tetrahydronaphthalene and subsequently fusing the sodium or potassium salt of the resulting sulfonic acid.

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[34] Brit. Patent [illegible]

[35] J. Soc. Chem. Ind., 41 (1922), [illegible]

[36] Ibid., 41 (1922), [illegible]

[37] J. Soc. Chem. Ind., 41 (1922), [illegible]

[38] Brit. Patent [illegible]

[39] [illegible] 3 (1921), [illegible]

[40] U. S. Patent [illegible]

[41] U. S. Patent 1,397,562.

[42] Brit. Patent [illegible]

[43] Brit. Patent [illegible]

[44] Annual Reports [illegible] 6 [illegible]

[45] Brit. Patent 169,732.

[46] Brit. Patent 147,964.

[47] U. S. Patent 1,394,851.

[48] THIS JOURNAL, **14** (1922), 406.

[49] Ger. Patents 338,683, 333,077, 330,824.

[50] U. S. Patents 1,314,924, 1,314,923; *Ber.*, **53** (1920), 78.

[51] U. S. Patents 1,314,925, 1,314,926, 1,314,924, 1,314,921, 1,314,922.

[52] U. S. Patents 1,314,928, 1,314,929.

[53] *J. Chem. Soc.*, **121** (1922), 715.

[54] *J. Soc. Chem. Ind.*, **40** (1921), 176T.

[55] *Ibid.*, **40** (1921), 176T.

[56] *J. Chem. Soc.*, **117** (1920), 241, 1574; Ger. Patents 299,603, 324,861, 305,104, 298,541, 298,553, 301,275, 336,615, 299,014, 326,486, 337,157, 316,218, 335,477, 335,602.

[57] Ger. Patent 317,634.

[58] British Patent 148,923.

[59] Brit. Patent 170,867.

[60] Brit. Patent 148,408.

ISATIN AND DERIVATIVES

By condensing aniline with chloraloxine in acid medium and ultimately warming the condensation product with sulfuric acid, isatin[61] results. In a similar way 4-chloromethoxyisatin[61] is produced from the hydrochloride of *p*-chloroanisidine. The 5-sulfonic acid of isatin, condensed with indoxyl, gives an indirubine[62] which dyes wool and silk a violet color. 6-Methylisatin, obtained from methyltoluidine and esters of mesoxalic acid, gives a substituted indigotin,[63] which dyes wool and silk but has only slight affinity for cotton. Many other such derivatives have been prepared and used to introduce desired groups in the indigotin molecule, but it does not appear that any of them have practical application.

NAPHTHOLS

Activity in this group has been largely confined to the improvement of existing processes for the manufacture of staple intermediates. It has been shown that losses in the manufacture of H acid[64] are caused by the formation of naphthalene-1,3,5,7-tetrasulfonic acid, to destructive oxidation and to the formation of 1,6- and 2,7-disulfonic acids which only sulfonate to the 1,3,6-trisulfonic acid with great difficulty. Some improvement is seen in the process for the naphtholsulfonic acids and anilides of β-oxynaphthoic acid. Anilides of cyclic acids are produced by heating acids of the cyclic series with anilides of acyclic acids, the acyclic acid being liberated. The 1,5,7-aminonaphtholsulfonic acid, M acid,[65] has been prepared and used as an intermediate in the manufacture of blue cotton dyes. Also, the 2-amino-5-naphthol-1-sulfonic acid, A acid,[66] has been used in certain combinations to give azo dyes.

NITRO COMPOUNDS

Attention is again directed to continuous nitration of benzene to mononitrobenzene by a process which uses mercury compounds as catalysts.[67] It is not clear from the available information what advantage the process has over other methods of nitration. Continuous operation of a process is not always advantageous.

Much progress has been made in the preparation of certain nitro compounds. The factors governing the nitration of phenolsulfonic acids to picric acid have been carefully considered and it has been shown that the best yield of picric acid is obtained when the sulfonation product of phenol contains over 80 per cent phenoltrisulfonic acid.[68] The yield varies with the proportions of mono- and disulfonic acids. The accumulation of SO_3H groups appears to stabilize the molecule or to inhibit oxidation during the nitration. Low yields are also often due to the presence of dinitrophenolsulfonic acids from incomplete nitration. Another process[69] sulfonates phenol to the disulfonic stage and then nitrates at about 30° to 40° C., while another process[70] proposes to nitrate the sulfonated phenol below 70° C. to the mononitrate product and then complete the nitration above 70° C. Trinitroresorcinol[71] has been obtained in a similar way by nitrating resorcinoldisulfonic acid suspended in concentrated sulfuric acid with 90 to 100 per cent nitric acid. *o*-Nitroanisol[72] is produced by boiling a mixture of o-chloronitrobenzene, methyl alcohol, potassium carbonate and an aqueous suspension of slaked lime. An interesting process for β-nitronaphthalene[73] consists in nitrating tetrahydronaphthalene, freezing out the β-nitro product from the first fraction distilled, dibrominating this and then vacuum distilling the resulting product to obtain β-nitronaphthalene. It is questionable whether β-naphthylamine can ever be made commercially from β-nitronaphthalene made in this way.

PHENANTHRAQUINONE AND RETENE

The utilization of phenanthraquinone and its derivatives has received some attention for several years but not until recently have the results appeared encouraging. Watson[74] and his co-workers have obtained dye intermediates from phenanthraquinone, the oxidation product of phenanthrene, by introducing substituents into the nucleus which serves to develop the condition essential for the manifestation of color and which makes possible dyeing properties. Phenanthraphenazine dyes[74] are obtained by condensing aminophenanthraquinone with *o*-phenylenediamine. Both wool and other dyes have been obtained—the 2,7 substituted phenanthraquinones give cotton dyes and the 4,5 derivatives, wool dyes.

Retene, methylisopropylphenanthrene,[75] is now available in large quantities as a pure product having been recently isolated from the high-boiling oils from pine tar. Diazonium compounds of retene have been prepared and converted into azo dyes[76] by coupling with naphtholsulfonic acids. Further work is necessary before any prediction can be made of the future of retene as a raw material for dye intermediates.

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[61] *Compt. rend.*, **172** (1921), 1234.

[62] *Ibid.*, **172** (1921), 330.

[63] *Ibid.*, **172** (1921), 220.

[64] *Helvetica Chim. Acta*, **4** (1921), 381.

[65] Fr. Patent 516,853.

[66] *J. prakt. Chem.*, **103** (1921), 129.

[67] U. S. Patent 1,380,185.

[68] *Bull. soc. chim.*, **27** (1920), 140, 199, 195, 370.

[69] *J. Am. Chem. Soc.*, **42** (1920), 2665.

[70] U. S. Patent 1,380,186.

[71] Brit. Patent 162,578.

[72] Brit. Patent 167,582.

[73] Ger. Patents 299,014, 332,593.

[74] *J. Chem. Soc.*, **119** (1921), 1211.

[75] Private communication.

[76] U. S. Patent 1,395,238.

Industrial Films

A six-reel motion picture film, "The Story of Steel," has been produced under the auspices of the Bureau of Mines and the Department of Commerce in coöperation with the United States Steel Corporation. It will be used extensively in the United States and abroad for the purpose of acquainting the peoples of the world with the many interesting operations employed in the American steel industry. The film depicts the various processes from the mining of the iron ore to the finished steel product. The manufacture of rails, plates, shapes, axles, rods, wire products, pipe, tin plate, and other products of steel is told in a graphic way, and before the picture is brought to a close the audience is shown the many welfare and social activities which are carried on by the United States Steel Corporation for the benefit of its employees. The film will be loaned without cost to all dependable persons desiring to use it for educational purposes. Application for its use should be made to the Department of Commerce, Washington, D. C.

"The Story of Natural Gas" has been produced by the Bureau of Mines in coöperation with the Natural Gas Association of America, and shows in an interesting and informative way the various steps in the development and utilization of natural gas supply, from the drilling of a gas well to the delivery of the gas to the consumer. The same Bureau has released "The Story of Oxygen," which was produced in coöperation with the Air Reduction Company. This picture shows, by the aid of animated cartoons, how pure oxygen is produced from air by liquefaction and expansion. This is followed by an exposition of the manifold uses to which oxygen is put in industry. Requests for the loan of these films should be addressed to the United States Bureau of Mines, 4800 Forbes St., Pittsburgh, Pa.

Under terms of a coöperative agreement with the Department of Commerce, the Pittsburgh Station of the Bureau of Mines also has available for distribution copies of the following films: "The Story of an Automobile;" "The Story of an Electric Meter;" "The Story of a Watch;" and "The Story of Compressed Air."

The motion-picture film, "The Story of Petroleum," prepared by the Bureau of Mines and the Sinclair Consolidated Oil Corporation, is to be exhibited in Jugoslavia and Czechoslovakia.

Science in the Textile Industry

By **E. D. Walen**

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IT IS ONLY within the last few years that we have heard very much regarding the application of research or science to that branch of textile industry devoted to the actual manufacturing of yarn and fabric. The chemist has already made tremendous strides in the application of basic principles to the finishing and dyeing part of the textile industry, and since it is so well started there has been perhaps less discussion of its advantages.

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The textile industry is one of the oldest and although it is not quite clear that cotton manufacturing is the oldest industry, it is, nevertheless, an ancient art which has grown to be of tremendous economical importance. An examination of the ancient textiles, such as those of Peru by M. D. C. Crawford, indicates strongly that there is very little new in the design of cloth and the construction of fabrics and yarns. A comparison of the quality of these yarns with the present-day yarns indicates that the greatest strides in the cotton industry have been along the lines of increased production and ease of manufacture, and we sometimes wonder if the basic principles of manufacturing have not been lost sight of to some degree.

The progress of science in the manufacture of textiles has been rather slow, and it is rather difficult, owing to the fact that the people engaged in the industry are hampered by the many generations of inertia; and in addition, the industry depends so much upon the existing machinery that it is difficult to conceive of valuable results until these machines have been substituted by those designed on new principles. Progress in other industries, however, has led many manufacturers to believe that there are possibilities in the application of the laws of natural science to the textile industry.

The governments of the several textile countries have maintained laboratories and scientific men for the investigation of cotton growing and to some extent cotton manufacturing, and much good has resulted from these studies. Perhaps the biggest research project that has gained any headway has been the British Cotton Industry Research Association, which dedicated its laboratories in the early part of this year. This association, we understand, is of a coöperative nature in that all British manufacturers are eligible to membership and the results are for their benefit.

In this country the formation of a large research body has been somewhat along different lines. Apparently, each association interested in cotton has a research section which varies considerably in its conception of research and in its activities. The National Association of Cotton Manufacturers, which probably represents the majority of cotton manufacturers in the country, has for some time maintained a research committee which has branched out into a research department. This department is still in its infancy and it is attempting to justify its growth by actual accomplishments.

The largest single project of individual research in this country was started in 1918 by the Lockwood, Greene & Company and the Pacific Mills interests. The first organization consisted of a committee which served as a clearing house of ideas for the several mills. This committee developed the fact that it was necessary to have a laboratory study the various problems, and in July 1919 the Cotton Research Company was incorporated. The stock ownership of this company was shared by the Pacific Mills and Lockwood, Greene & Company. It was planned to allow the company to operate for a probationary period, in order to give the project a fair chance to prove its value. This period has passed and the project is believed to be worth while continuing.

The company is essentially an industrial laboratory and it was not thought at first that it would be necessary to engage along the lines of pure research, but it has been interesting to note that as the work has progressed the demand for the solution of problems along basic lines has steadily increased and the practical mill man has been found to be more interested in knowing the underlying cause than in knowing the immediate effect.

The original equipment consisted of much textile machinery for conducting tests and very little laboratory equipment for the study of the samples prepared. Since that time about 50 per cent of the machinery has been disposed of and the laboratory equipment enlarged. The laboratory equipment available for the study of manufacturing is extremely limited, and it has been found necessary to design and construct all of it.

The organization of the company has been built up around four groups:

1—The directors, who represent the financial interests and determine the policies along broad lines.

2—An advisory council, composed of mill agents and superintendents of the various mills interested, who convene at intervals to discuss the policies and to determine the scope of the immediate problems.

3—A group trained along the scientific lines of physics, chemistry, and microscopy.

4—A group of practical men trained in the laboratory to conduct tests who are familiar with the application of laboratory developments as applied to the study of manufacture.

The activities have been built up around the study and maintenance of quality and the economy of manufacture, and all the developments are necessarily focused on the mills as soon as they become of value. The adaptation to the mill is carried on by the group of practical men and the advisory council.

It has been necessary in a program of this sort to develop methods for accurately and quickly measuring the physical properties of the raw materials. The immediate application of such measurements is interesting from the viewpoint of the selection of proper types of cotton, the probable value of new crop cotton for yarn made at a particular plant, study of the efficiency of a manufacturing operation from the viewpoint of the raw product, tracing the cause of poor yarn, and the application of correct measurements based upon accurate knowledge of cause.

Contrasted to this study and application there is another important study based on the assumption that an industry as old as the cotton industry must have in each mill a number of good features. This involves the careful noting of all details of the factors of production and quality, a proper analysis, and adaptation of the good points to the mills concerned.

The photomicrographic analysis of materials has been of the greatest help in recording arrangement of fibers, uniformity, effects of settings, degree of dye and size penetration, balance of structure, and many other things which are important but not discernible to the naked eye.

Our activities along the chemical lines have been rather limited and have been confined largely to the study of warp sizing. This problem has been considered as a problem in physics, using chemistry as a means of designating the materials.

We believe that much progress has been made and that the results warrant the existence of a research organization, but the surface has hardly been scratched and developments in the future years are bound to be nothing short of phenomenal.

Heat Treatment Progress during 1921

By A. E. White

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THE PROGRESS of ferrous metallurgy, especially that closely allied with the heat treatment of steel, has shown no outstanding milestones this past year, progress having been one of refinement and lacking in spectacular accomplishments in matters of materials, equipment, and in the character of the personnel employed.

With regard to materials, there has been a growing interest in the developments of heat-resisting and nonoxidizing alloys. There is daily a greater appreciation that we must have alloys which will withstand oxidation and deformation at temperatures higher than the normal atmospheric temperatures; also that we must encourage the use of alloys that at high temperatures retain to the greatest degree a proper combination of strength and ductility. The use of carburizing boxes that will withstand warpage and oxidation under the conditions of service to which such boxes are subjected has received considerable attention. One of the recent alloys brought out for this general purpose is known as *Calite*, composed essentially of nickel, aluminium, and iron.

The structural material that has received the greatest consideration this past year, though not of this year's development, is molybdenum steel. It is an alloy steel comparable to our nickel steels, chrome-nickel steels, and chrome-vanadium steels. Practice seems to indicate that the chrome-molybdenum type is an acceptable forging steel, and that the nickel-molybdenum type is a satisfactory case-hardening steel.

In the matter of equipment used for the heat treatment of steel, there have been no outstanding developments, though many plants throughout the country have made changes in furnaces and furnace appliances which go a long way toward placing the heat treatment of steel on a scientific basis. Pyrometric control is now available so that temperature in the furnace is no longer subject to the variations of manual control. This pyrometric control, at one time only possible in electrically heated furnaces, is now possible in both gas-fired and oil-fired furnaces. There also is a growing tendency toward the use of conveyor type furnaces, and this in turn tends to eliminate the human factor. Combined with all these facts is an increased use of fixtures for quenching, better designs of furnaces to secure more uniform temperature in the same furnace, and better refractories, resulting thereby in a decided reduction in maintenance costs.

Combined with all of these factors the personnel in the heat treatment departments of the various plants throughout the country has improved. This has been due in some measure to the depression, since only the better men were retained and they realized that in order to hold their positions they must operate as intelligently as possible. In the heat treatment rooms there are many college-trained men, and large numbers of the others have had at least a high school education. These men are keen to absorb new ideas and new methods, and they appreciate also that to procure them they must exchange ideas. This broadmindedness on the part of those engaged in the steel heat treating field has no doubt been one of the reasons why it has developed so rapidly. There are but few shops in the country that prevent their men from freely exchanging ideas with their fellows.

An appreciation on the part of our technical societies that their function is in large measure the bringing together of the technically trained men and the operatives whose advantages in their given field have not been as great, has been of no little moment in the advance of the art of heat treatment.

Numerous investigations in this general field are under way. On some, preliminary reports have already been made, whereas on others the work has not progressed to a degree warranting publication. Some of the most outstanding investigations are: The work of Professor Moore and his colleagues on "The Fatigue of Metals," the work in progress on "Drill Steel" under the combined auspices of the United States Bureau of Mines, the American Institute of Mining and Metallurgical Engineers and others; and the work of the U. S. Bureau of Standards on:

1—Gage steels.

2—High temperature tests of commercial steels.

3—Proper mixtures for use in selective carburization.

4—A suitable method for the measurement of hardness in hardened steels.

5—The use of magnetic testing for the determination of uniformity in steel.

Heat Transmission and Evaporation

By W. L. Badger

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There is scarcely a process with which the chemical engineer is concerned that does not involve the transfer of heat in some form. In a great variety of circumstances he must pass heat through a separating wall with sometimes liquids, sometimes vapors, and sometimes permanent gases on either side. But if he wishes to design such apparatus intelligently and accurately he finds the literature practically devoid of information that might help him.

W. L. Badger

This has come about for several reasons. The fundamental principles of heat transfer (such as the fact that it is proportional to temperature drop) have long been familiar; but though more than a generation ago the variables which affect heat transfer were thoroughly discussed, only a couple years ago an engineer stated in the proceedings of an important society that since copper had seven times the thermal conductivity of iron, an evaporator with copper tubes should do seven times the work of one with iron tubes. Actually, while a plate of copper 0.1 in. thick and 1 ft. sq., with a difference of 1° F. between the two sides, will transmit about 25,000 B. t. u. per hr., a layer of water 0.01 in. thick on each side will reduce this to about 200 B. t. u. The resistance of the copper will then be only about 1/150 of the total, and the substitution of iron for copper would have practically no effect. This film concept as applied to heat transfer has been more or less recognized for about 30 yrs., and other factors, such as the effect of viscosity, circulation, elevation of boiling point, hydrostatic head, etc., were recognized even further back; but the number of engineers who fully appreciate the significance of these factors is disappointingly small.

A series of heaters were designed by a man well known in his field of engineering and installed in a plant operated by graduate mechanical engineers. The heaters were not doing what they should and the writer was called on to revise the equipment. It was found that each heater had three hundred and sixty $2^1/_2$-in. tubes, all in one pass. The amount of material being circulated was such that its average velocity was about 0.1 ft. per sec. Inquiry developed that neither the designer nor the operating engineers had ever thought of figuring liquid velocity.

While we may expect to see in the near future a certain amount of information in fairly satisfactory shape on heat transfer when heating liquids or gases, we will have to wait a long time for information on evaporation. When a liquid is actually boiling, conditions are so complex that as yet they have defied mathematical analysis. The evaporator, whether single or multiple effect, is one of the chemical engineer's most important tools, yet we really know very little about it. [illegible] us just short of being able to [illegible] evaporator, and constants are almost wholly lacking. Even the standard types still need much study.

If one attempts to list the particular points in which progress is being made in this field, he must first admit that so far as general engineering practice is concerned, the last few years have seen little change. Rising coal prices have thrown the weight of opinion toward triple or quadruple effect evaporators, where before the war the double effect was most common. Mechanical engineers have made progress in the design of surface condensers and their auxiliaries. A few new ideas have been advanced, notably that of recompression of vapors, but this is not yet commercially feasible in this country. At the University of Michigan we are trying to make some headway on a study of evaporator theory. The Massachusetts Institute of Technology has published some beginnings of a study of real film coefficients. Some of the larger corporations are making tests and developing new ideas, but this work is rarely made available by publication. Perhaps the most promising feature is the increasing number of engineers who are really thinking accurately about heat transmission problems, and who are coming to realize the need for work in this field.

Our work at the University of Michigan is only beginning and is as yet largely empirical. The writer has literally dozens of problems in connection with standard evaporator design which have not yet been touched; and if one also considers the possibility in the way of new types, the field is correspondingly broadened. For instance, the average evaporator operates with a heat transfer coefficient of somewhere from 100 to 400 B. t. u. per sq. ft. per hr. per ° F. Feedwater heaters may, under special conditions, reach 1000 to 1100 B. t. u. The writer has seen a special evaporator in operation for which 1500 to 2000 B. t. u. are claimed. This was accomplished by accepting the film concept and attempting to scrape off the film.

The problems now facing us are varied. How can we predict accurately the temperature distribution in a multiple effect evaporator? What are the exact effects of such factors as viscosity, circulation, hydrostatic head, etc., on the film coefficient between boiling liquids and metal surfaces? What is the effect of superheat in steam on heat transmission? Why do salt crystals grow on the heating surfaces instead of in the solution? If we turn to artificial circulation, where shall we find increased heat transmission offset by cost of stirring? What is the field for re-use of vapors by recompression? Where are we to get the physicochemical data (such as elevation of boiling point, solubility, specific gravity, specific heat, latent heat of evaporation, etc.) for the strong solutions which we use in practice and which the physical chemist has not considered because they fail to follow his laws for dilute solutions? Several of these problems we have already attacked, and on one or two we have made considerable progress. There is plenty of room, however, for more workers.

Besides the vast amount of experimental work yet to be done, there is much ahead of us in educating engineers to think in terms of the heat balances of a plant as a whole.

Few engineers outside of the sugar industry appreciate what can be done by a proper interlocking of power units, evaporating units, and heating units. Such economies are possible, when this group of operations is considered as a whole as no power specialist and few heating or evaporating specialists realize. For instance, in beet-sugar manufacture, 12 to 15 per cent coal is burned (calculated on the weight of the beets) in the best practice in this country. It is said that 9 per cent is reached in Germany, but German mills do not produce a finished sugar. There is a mill in this country which was well built by a good sugar engineer. It has been operated for some years by wholly untrained superintendents. Owing mainly to a lack of knowledge of how to coördinate the power, heating, and evaporating units, the fuel consumption has risen year by year (as the original design in the mill has been altered) until last season it used 25 to 30 per cent coal on the weight of the beets.

There are many other similar fields in chemical engineering which need extensive work. Practically all of the unit operations are in the same state as heat transfer. Distillation and drying are receiving considerable attention at present. Mixing and stirring have not been touched; filtration has been worked on only enough to outline the problems; in fact, chemical engineering, as such, is still in almost every phase a new and undeveloped field.

The Vegetable Oil Industry

By David Wesson

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THE PAST two years have brought to light few, if any, great changes in products or manufacturing methods, though a great deal has been done toward improving existing methods with a view of securing greater economy of operation and improvement of product.

In the matter of solvent extraction there has been considerable progress in Europe. In England there is a large plant operating on palm kernels and copra, producing upward of 80 to 100 tons of edible oil per week. In this country one or two large plants, which were highly successful during the war, have closed down on account of peace conditions.

The manufacture of by-product coke has made available large quantities of benzine at a reasonable price. This is an ideal solvent for peanuts, copra, palm kernels, and other seeds that are free from coloring matter. The petroleum people are giving attention to the production of a fraction with low boiling point distilling within close limits, also suitable for this purpose.

The literature discloses twenty or more patents mostly relating to apparatus. A novelty is the proposal by McKee to use sulfur dioxide as the extraction medium.[1]

In refining the oil various innovations have been presented for removing the free fatty acids in such a manner as not to saponify neutral oil or carry out the same with the soap formed in the usual method of saponification.

E. R. Balton and E. J. Lush[2] convert free fatty acids into glycerides by heating to 200° to 250° C., and treating with glycerol vapor. They claim that the resultant neutral fat can be refined.

H. Schlinck and Company[3] neutralize the fatty acids by boiling the fat containing same with glycol under a reflux condenser using 11 per cent glycol by weight of the fatty acids present, and removing the water formed by operating in vacuum or passing an inert gas. They also add a suitable catalyst and pass hydrogen to hydrogenate at the same time.

C. and G. Muller Speissefett fbr. A. G.[4] dissolve the fat in a solvent miscible in water, such as acetone, then add sufficient water to precipitate the neutral, leaving the fatty acids in solution. The solution of fatty acids is drawn off and more water added to precipitate them.

L. Schmidt[5] dissolves the oil in a suitable solvent, then agitates with alkali and removes the resultant soap by filtration. The process is said to be operated in Switzerland, Italy, and Germany.

The bleaching of oils for edible purposes continues to be done mostly with fuller's earth, with or without the addition of bleaching carbons in some of the various forms. A large variety of fuller's earths are now on the market. Most of them are natural products prepared by drying and grinding, while others are made by action of sulfuric acid on suitable clays. Some of these artificial earths have marked bleaching properties.

The past two years have witnessed a large number of new bleaching carbons mostly of vegetable origin, made by the treatment of waste materials. Some of them pound for pound are far more active than boneblack, but their increased activity is largely offset by advanced price.

David Wesson

This operation of hydrogenation seems to be pretty well standardized, though numerous patents have been taken out on apparatus and catalysts. Electrolytic hydrogen seems to have been pretty generally adopted. The low prices of hard animal fats have largely curtailed the output of hydrogenated oils.

Vitamins have been very much in the limelight the past two years. Many new facts have been discovered and many of the previous exaggerated ideas exploded.

Dr. H. C. Sherman in his recent work, "The Vitamins," published by the Chemical Catalog Co., gives a fair summing up and classification of most of our knowledge to date on this matter, so voluminous in the literature and so meager in exact chemical facts.

Dr. Casimir Funk in an address before the Institute of Margarin Manufacturers, published in *The American Food Journal* for June 1922, points out the deficiencies of the fat-soluble vitamin in butter fat in the case of rickets and shows that cod-liver oil contains fat-soluble vitamins in much higher concentration than they occur in butter fat. He also indicates recent researches in analytical methods which extend the hope that we may soon be able to identify the different bodies.

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[1] U. S. Patent 1,376,211.

[2] Brit. Patents 159,587, 163,352 (1919).

[3] Ger. Patents 334,659, 315,222 (1916).

[4] Ger. Patent 339,027 (1918).

[5] U. S. Patent 1,395,998 (1921).

The Department of Agriculture has started a comprehensive research on cottonseed and the products therefrom, in coöperation with the Interstate Cottonseed Crushers' Association. Drs. Jamieson and Baughman of the Bureau of Chemistry have already published a method for the analysis of crude vegetable oils, giving the amount of absolute oil obtainable from any sample of crude by alkali refining. The published results show that in refining crude oils by alkali, only 95 to 96 per cent of the available refined oil is obtainable in factory operations with existing methods. Work is now being done to separate and identify the various impurities present in the crude oil and to determine their effect on losses and quality of the refined oil. The same writers have also published analyses of cottonseed and peanut oils prepared from authenticated seeds from many localities and pressed under known conditions in the laboratory. These results give us the variations in the chemical constants of these oils and are far more reliable than those commonly published in the literature. For a full statement of the work done by the Bureau of Chemistry, the reader is referred to a very able article by Dr. W. W. Skinner in the *Chemical Age* for June 1922.

Considerable work has been done toward more accurately describing the colors of vegetable oils. A progress report of the Committee on Color of Oil and Seed was presented before the June meeting of the American Oil Chemists' Society. The report showed a highly improved colorimeter recently brought out by the Eastman Kodak Co., which makes it easily possible to report on the color of oils in the terms of yellow, red, and neutral tint or darkness. It is also possible to obtain color matches impossible with previous methods.

The same report gave a description of the color analyzer just perfected by Keuffel & Esser, whereby it is possible to obtain a spectrophotometric curve of any sample of oil, and from the curve to determine whether it has been put through various refining processes. It also shows the difference in color between different oils. The instrument, needless to say, adds greatly to the facilities for research.

The constant requirements in manufacture call for more exact chemical information and methods, and call for travel on a little explored field. In the analyses of the oils themselves, we can separate the various fatty acids of the mixed glycerides; but what do we know of the mixed glycerides themselves, and their structure? It is highly desirable that methods should be devised for separating the different glycerides, both for analytical information and the proper control of manufactured products. This is particularly true in the industries dependent on hydrogenation. We may know the proportion of different fatty acids present, but have little more information regarding the structure of the fat and its resultant properties, than we could obtain regarding the design of a building by studying the bricks and stones constituting its [illegible].

In the operating of bleaching oil by fuller's earth, we know little regarding the properties of the color removed, or just what action the earth has on the oil. We do know that the earth apparently oxidizes and polymerizes a portion of the oil and removes the same in addition to the color, but why and how we know not.

In deodorizing the oil by steam, certain malodorous principles are distilled off. It is not improbable that these might be developed into desirable perfumes.

In the extraction of crude oil by pressure, about 15 per cent of the total remains behind in the press cake. We know that it can be removed by solvent extraction. It is simply a question of mechanical and chemical research to substitute solvent extraction processes for the clumsy hydraulic presses. Solvent extraction produces choice oils in the laboratory, and with suitable apparatus can do the same in the factory.

The factors involved in the rancidity of fats and best means for preservation are important subjects for research of great practical value.

Each of the separate problems mentioned above resolves itself into many minor ones, so it may safely be said that the field of research in the edible fat industry is still a large one and well worthy of cultivation.

Solvent Extraction of Vegetable Oils

By C. F. Eddy

Research Associate, Research Laboratory of Applied Chemistry,
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THE STRESS of war conditions gave the solvent extraction industry a big impetus, especially in Europe.[1,*] The success obtained has helped to break down prejudice and has stimulated investigation and discussion.

C. F. Eddy

The higher yields obtainable by solvent extraction are clearly shown in a table given by Shrader,[2] and Pickard's report[3] that in five normal years before the war a solvent extraction plant for flaxseed gave a net return of $1.50 per ton of raw material more than for a similar pressing plant, shows that the advantage is not merely theoretical.

Thiele[4] has recently pointed out another advantage of this higher extraction of oil. When the oil has developed an appreciable amount of free fatty acids, a very low oil meal will be free from objectionable rancidity. In this connection, some have claimed that the steaming necessary to free the meal from solvent also increases its value for feed purposes.

Another advantage of the solvent extraction method that is being developed is in connection with the removal of free fatty acids from the extracted oil. In refining by the same method samples of pressed and solvent-extracted cottonseed oil, Shrader reports[5] refining losses for the extracted oil much less than for the pressed oil. In a previous article[6] he refers to having tried Dr. Wesson's suggestion of refining the oil in solution instead of refining after the solvent had been removed. The only observation made was a comparison of the color of the oils refined by the two methods. If he was aware of the much greater simplicity of apparatus and method possible with refining in solution he did not mention it, and others have secured patents on the method.[7,8]

The developments of processes and new types of apparatus[17–23] have been very numerous, but some of them, especially some unpublished ones, have been great improvements.

[*] Numbers in text refer to Bibliography at end of article.

With the proper apparatus, fire hazards,[4] dangers of poisoning to workmen,[9,10] and solvent losses are being greatly reduced, if not eliminated.

Unfortunately the apparatus or process that is the best for one oil is not necessarily the best for another, and poor judgment in selecting apparatus or process has resulted in many failures. Then, even if research has shown the proper apparatus and method to be used and a prime product is produced, there is no question but that many a hesitant buyer will swear that he tastes solvent in the product. Sievers reports[11] troubles with samples of benzol-extracted corn oil that recall similar experiences. The author and others with whom he has compared notes have slipped in samples of pressed oil with solvent-extracted samples and had men swear they tasted solvent in all of them. Masahiro Aida[12] has given a test for minute quantities of petroleum spirit in vegetable oils and there should be a test for small quantities of the more commonly used benzol to settle the argument when there is any doubt.

It sometimes happens that the steam distillation necessary to remove the last traces of solvent will also remove some of the characteristic odor or flavor of the oil, leaving a more neutral or flat taste. Once again the buyer may hesitate because it is not what he is accustomed to.

Further research along certain lines is absolutely essential if solvent extraction is to fulfil the expectations of its advocates. Such moot questions as the proper solvent to use for certain oils, the effect on the color and taste of the oil if hulls or shells are present during extraction, the effect of the metal of the extractor on the finished product, etc., must be answered sooner or later if the industry is to progress.

With the improvements constantly being made in processes and in apparatus, and with the light that is being thrown on the subject by careful study and discussion, added weight is given to Pickard's conclusion[3] "that the future of the vegetable oil industry lies in the adoption of the extraction process."

BIBLIOGRAPHY

1—A. V. De Ford, "European Solvent Extraction Process," *Cotton Oil Press*, **5**, No. 1 (1921), 61.

2—J. H. Shrader, "Solvent Extraction in the Vegetable Oil Industry," *Chem. Met. Eng.*, **25** (1921), 94.

3—G. H. Pickard, "Solvent Extraction of Vegetable Oils," *Cotton Oil Press*, **5**, No. 2 (1921), 119.

4—L. A. Thiele, "Solvent Extraction in the Production of Oils and Fats," *Chem. Age (N. Y.)*, **30** (1922), 65.

5—J. H. Shrader, "Further Studies on Relative Quality of Expressed and Solvent Extracted Cottonseed Oil," *Cotton Oil Press*, **4**, No. 12 (1922), 29.

6—J. H. Shrader, "Relative Quality of Expressed and Solvent Extracted Cottonseed Oil," *Cotton Oil Press*, **4**, No. 12 (1921), 42.

7—Rocca, Tassy and de Roux, "Refining in Solution," Brit. Patent 153,887 (1920).

8—W. Gleitz, "Refining in Solution," U. S. Patent 1,408,804 (1921).

9—A. Hamilton, "Industrial Poisoning from Compounds of the Aromatic Series (Benzene)," *J. Ind. Hyg.*, **1** (1919), 200.

10—L. Lewin, "Toxicity and Poisoning Symptoms of Solvents Used in Extraction," *Z. deut. Ol- Fett-Ind.*, **40** (1920), 421, 439.

11—A. F. Sievers, "Comparison of Corn Oils Obtained by Expeller and Benzol Extraction Methods," *U. S. Dept. Agr.*, *Bull.* **1054** (1922).

12—Masahiro Aida, "Detection of Minute Quantities of Petroleum Spirit in Vegetable Oils," *J. Soc. Chem. Ind.*, **39** (1920), 152T.

13—Pollatschek, "Extraction of Oil Cakes," *Z. deut. Ol- Fett-Ind.*, **41** (1921), 1.

14—Anon, "Vegetable Oil Manufacture," *Chem. Age (London)*, **5** (1921), 449.

15—H. J. Pooley, "Solvent Extraction for Vegetable Oils," *Chem. Age (London)*, **4** (1921), 724.

16—J. H. Shrader, "The Castor Oil Industry," *U. S. Dept. Agr.*, *Bull.* **867** (1920).

17—S. Sato, "Proteins of Soy Beans and Their Industrial Applications," *J. Chem. Ind. (Tokyo)*, **22** (1919), 851.

18—Anon, "Treatment of Oil-Bearing Products," *Chem. Age (London)*, **4** (1921) 614.

19—Yamomoto, Morimoto and Moriyama, "Apparatus for Extracting Oils," Japan Patent 36,328 (1920).

20—L. C. Whiton, "Extracting Fats," Brit. Patent 143,196 (1920).

21—M. Wilbuschewitsch, "Extracting Oils," Brit. Patent 147,745 (1920).

22—J. Martin, "Method of Extracting Soy Beans by Means of a Solvent," *Mat. grasses*, **13** (1921), 5879.

23—O. Kausch, "Oil and Fat Extractors," *Z. deut. Ol- Fett-Ind.*, **42** (1922), 4, 23, 37, 61, 100, 123.

24—A. F. Sievers and T. D. McIntyre, "The Relative Effectiveness of Several Organic Solvents for the Extraction of Vegetable Oils," *Cotton Oil Press*, **4**, No. 10 (1921), 44.

25—S. Ochi, "Extraction Power of Carbon Tetrachloride for Fatty Oils," *J. Chem. Ind. (Tokyo)*, **22** (1919), 1067.

26—H. Bollman, "Refining with a Solvent," Brit. Patent 164,115 (1920).

The Trend of Prices

In the June number of the *Chemical Bulletin* S. L. Redman makes a comparison of 1913–1922 foreign and domestic prices of typical chemical apparatus. He summarizes the situation as follows:

> To sum up briefly, there has been a continued downward trend in the price of laboratory supplies during the past eighteen months, except in those staple lines of glassware and porcelain whose prices remained stationary during the war and post-war period of rising costs. Prices will probably continue to recede gradually throughout a period of years until the pre-war level is reached. Special instruments, whose cost of development was very high, were introduced at rather high prices and, as the process of manufacture has been perfected, generous price reductions have been made. No immediate relief is to be expected from the importation of German goods, since the difficulties experienced by German manufacturers with raw materials purchased with a depreciated currency, with restricted fuel supplies and labor troubles combine to make prices higher than those of the corresponding grade of American-made materials. Chemical prices reached bottom last year and if any change occurs in the near future, it will probably be in an upward direction.

These conclusions are based upon the following tables:

RETAIL PRICES

	1913	1919	May 1922	Aug. 1922
Evaporating dish, No. 0	$0.19	$0.24	$0.24	$0.23
Griffin beaker, 250 cc	0.22	0.25	0.25	0.25
Florence flask, 400 cc	0.24	0.27	0.27	0.24
Cylindrical graduate, 100 cc	0.50	0.63	0.60	0.57
Thermometer, 110° C	0.80	1.20	1.10	1.05
Bunsen funnel, 3 in	0.18	0.43	0.35	0.35
Soxhlet extraction apparatus, 100 cc.	2.70	3.85	3.80	3.50
Bunsen burner	0.22	0.45	0.35	0.35

COMPARATIVE PRICES (May 1, 1922)

	American-Made (Coors, Pyrex, Taylor, etc.)	German-Made (Royal Berlin, Jena, Siebert & Kuhn, etc.)
Evaporating dish, No. 0	$0.24	$0.35
Griffin beaker, 250 cc	0.25	0.25
Florence flask, 400 cc	0.27	0.32
Cylindrical graduate, 100 cc	0.60	0.80
Thermometer, 110° C	1.10	1.10
Bunsen funnel, 4 in	0.44	0.38
Soxhlet extraction apparatus, 100 cc	3.80	4.00
Globe-shape separatory funnel, 250 cc	1.65	2.15

Instruments differ so widely in characteristics that it is difficult to draw any comparisons as to makes. The tendency toward lower prices, however, may be illustrated by taking the Abbé refractometer. A well-known American manufacturer developed one of these two years ago which sold at a retail price of $425. About a year ago, the price was reduced to $320, and just recently to $275. Another American maker has placed an Abbé refractometer on the market at a price of $250. The first American-made saccharimeter retailed two years ago at $710. This was later reduced to $525.

Platinum Theft

The chemical laboratory of the Westinghouse Electric & Manufacturing Co., East Pittsburgh, Pa., has recently lost the following pieces of platinum:

	Weight
One dish	32.2450 g.
One dish	40.2720 g.
One crucible	36.8328 g.
One crucible marks No. 8 and Ⓑ	18.0254 g.

Local Anesthetics

By Henry Gilman

Department of Chemistry, Iowa State College, Ames, Iowa

THERE are two main classes of anesthetics: general, where the patient suffers temporary loss of consciousness; and local, when the patient retains consciousness during the operation. General anesthetics may be inorganic or organic compounds, such as nitrous oxide, ether, chloroform, ethyl chloride, etc. Local anesthetics may be inorganic or organic compounds, but organic compounds are used almost exclusively.

The history of local anesthetics is intimately and for a time was altogether associated with cocaine, which substance was introduced in local anesthesia about forty years ago. Without entering into a discussion of the relative merits of general and local anesthesia, it is sufficient to remark that statistics indicate a steady growth in the use of local anesthetics for both minor and major operations.

Henry Gilman

Need of Substitute for Cocaine

In surgery, particularly in dental work, cocaine, has been rather largely superseded by synthetic local anesthetics. The reasons for this are several and concern themselves with inherent comparative disadvantages of this naturally occurring alkaloid. First, cocaine is relatively more toxic or poisonous than some commonly employed synthetic compounds. Second, cocaine is a habit-forming drug and carries with it the added disadvantage of such drugs—the need of conforming with the proper legal exactions of the Harrison narcotic law. Other disadvantages are often cited, but these two may be considered as of prime import.

Substitutes for cocaine (and we here refer to synthetic organic compounds) should satisfy the following requirements:

(1) They must be less toxic than cocaine in proportion to their local anesthetic action.

(2) They must not cause irritation or tissue injury, and largely for these reasons compounds that react strongly acid or alkaline are not used.

(3) They must be water-soluble, and give solutions sufficiently stable to be sterilizable by boiling.

(4) They must be compatible (possible of mixing without serious alteration) with adrenalin. Adrenalin is an organic compound obtainable from the suprarenal glands and is also prepared synthetically. It has the extremely valuable property of constricting blood vessels. This not only renders the tissues of an area comparatively bloodless during operation, but also increases local anesthesia and decreases the general toxic action by reducing the rate of absorption by the system.

(5) For particular operations involving mucous membranes they must be able to penetrate rapidly.

For such mucous membrane work as eye, nose, and throat the anesthetic is applied topically, being absorbed directly from a wad moistened with the compound. For most other work the solution is injected. The cost factor, on the whole, is not always of major consequence: someone has made the trite remark that although ether is more expensive than chloroform in general anesthesia it is less costly than a funeral.

The success which has attended the efforts of organic chemists in this field has naturally developed from the methods of attack, which have been followed in the solution of related problems.

Essentially this is the problem. Cocaine is a naturally occurring organic compound with certain physiological properties, particularly that of producing local anesthesia. It has some inherent defects which must be remedied or circumvented. Inasmuch as cocaine is a pure organic compound this involves either an alteration of the cocaine molecule or the synthesis of new compounds having at least the desirable properties of cocaine with few or none of its disadvantages.

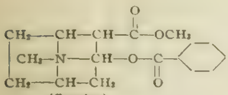
Method of Attack

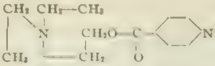
With such problems the first procedure is one of analysis. This involves in order: separation and purification, qualitative analysis, quantitative analysis, and molecular weight determination. From these the molecular formula can be obtained. The work has only begun, for the molecular formula alone is essentially worthless with complex organic compounds, such as cocaine, $C_{17}H_{21}O_4N$. The structural or constitutional formula, which shows the manner of arrangement of atoms and groups in the molecule, must next be determined. This is arrived at by a process of analysis or fragmentation, the breaking down of the molecule by standard reactions into reasonably large parts which are isolated and then identified by reference to previously known compounds. Generally, this structure is confirmed by a synthesis using known compounds and standard or reliable reactions.

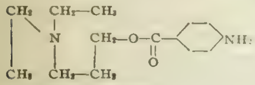
That which follows is essentially empirical at first. Alterations are made in the disposition or arrangement of groups in the molecule, in the kind, and number of groups. After each new compound has been made it is pharmacologically tested, at first on lower animals, to determine the effect of such changes on the physiological properties. In this way we arrive at certain rules or generalizations which serve to correlate physiological action with chemical constitution. With new drugs this involves the synthesis of many new compounds, first, in order to determine the effect of variations in structure, and second, if we would synthesize a substance with optimum physiological properties. A large proportion of these compounds may appear to be of doubtful value. The method is orderly, rational, scientific, and, for the present, inevitable. Arsphenamine, or "606," the organic compound so widely used in syphilis and allied diseases, is one of the most important drugs the world now has and only came into being after Ehrlich had previously prepared 605 solutions.

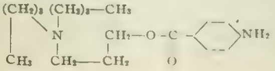
Procaine

Following the methods of procedure just indicated, chemists have synthesized a number of organic compounds whose physiological properties have warranted their rather wide adoption in medicine. Foremost among these compounds is procaine, formerly known in this country as novocaine. It is the hydrochloride of the *p*-aminobenzoate of β-diethylaminoethyl alcohol. The hydrochlorides of these basic compounds are generally used, but for convenience the free bases are graphically presented for comparison.


(Cocaine)


(Procaine)


(Kamm's compound)


(Butyn)

It will be observed that procaine bears some structural resemblance to cocaine. There are a few essential differences. Procaine is simpler in the sense that it has not the "bridges" or cyclic structures so characteristic of cocaine. There is also a para-amino group in the benzene nucleus of procaine. A third difference is in the number of carbon atoms between the nitrogen and oxygen atoms. In cocaine there is a chain of 3 carbon atoms between the nitrogen and oxygen atoms, whereas in procaine there is a chain of only 2 carbon atoms between the corresponding nitrogen and oxygen atoms.

Kamm[1] forecasted that the introduction of another carbon atom between nitrogen and oxygen would give a compound whose physiological action would be intermediate between that of cocaine and procaine. This prediction of the action of a new compound by analogy to structures of known compounds was admirably substantiated. The compound, recently synthesized by Kamm, was found to be slightly more toxic than procaine but less toxic than cocaine; it was more effective for surface anesthesia than procaine but less effective than cocaine.

BUTYN

Here, then, was a valuable clue for the synthesis of a compound that was to have the excellent property of cocaine for surface anesthesia. This property of surface penetration has limited the application of procaine in mucous membrane work. The need of such a compound in eye, nose, and throat work was urgent. As a result of the elegant synthetic work of Adams, Kamm and Volwiler,[2] butyn was prepared; it was selected as the best drug from some 40 compounds made by them. After a thorough and eminently satisfactory series of clinical tests, the compound is now used for mucous membrane work. Butyn is the sulfate of the *p*-aminobenzoate of γ-di-*n*-butylaminopropyl alcohol. This compound is probably the most important local anesthetic recently prepared. It is distinctly an American product, and was made possible by the excellent collaboration between the university, the drug house, and the physician. In passing, it might be mentioned that unpublished results indicate butyn to be less toxic than cocaine even when injected in man.

Other work has been done recently with compounds related to procaine. In a study of the effect of unsaturated groupings on local anesthetic action, Braun and Braunsdorf[3] have replaced one of the ethyl groups in procaine by an allyl group, and by a cinnamyl group. Both compounds were found to have a stronger anesthetic action than procaine. V. Braun has made many important contributions to our knowledge of local anesthetics and this is his most recent work. Prior to this Kamm and Volwiler[4] prepared the diallyl analogs of procaine and butyn. Osterberg and Kendall[5] have prepared the *o*-diethylamino-cyclohexanol ester of *p*-aminobenzoic acid, a homolog of procaine with larger molecular weight. No report has yet been made on the physiological action of this compound. Mention should be included here of apothesine, the cinnamate of γ-diethylaminopropyl alcohol, a product of American origin introduced during the war and used quite extensively.

ANESTHESIN

Another class of local anesthetics insoluble in water but used in powder form includes anesthesin, the ethyl ester of *p*-aminobenzoic acid. Brill[6] has prepared a series of related esters one of which, the *n*-butyl ester of *p*-aminobenzoic acid, is the subject of a patent by two drug manufacturers, one American and one French. Thoms and Ritsert[7] have studied the effect of replacing one of the amino hydrogen atoms of anesthesin by various positive and negative groups. Only in the case of ethyl *p*-hydrazinobenzoate, where a second amino group was substituted for a hydrogen atom, was the anesthetic action comparable with that of anesthesin. Altwegg and Landrivon[8] have patented the β-haloethylaminobenzoic esters and the corresponding compound obtainable by replacing the halogen by the diethylamino group. Adams and Volwiler[9] have prepared the allyl-*p*-aminobenzoate.

BENZYL ALCOHOL

Another class of local anesthetics owes its origin to the researches of Macht,[10] who, in connection with a study of the physiological action of various alkaloids, examined the anesthetic properties of benzyl alcohol and some of its simple derivatives. This field has been worked almost exclusively by Americans. Benzyl alcohol is used to a slight extent as a local anesthetic. A number of local anesthetics have additional valuable properties, such as antiseptic action and narcotic action. In this connection it should be said that various esters of benzyl alcohol are very useful as anti-spasmodics. Recent work has indicated a close, but not complete, correlation between the anti-spasmodic action and the rate of hydrolysis of these benzyl esters.[11]

OTHER LOCAL ANESTHETICS

The success of Macht and co-workers with benzyl alcohol has served to extend our knowledge of the local anesthetic properties of related compounds. Hjort and collaborators, in a study of various aromatic alcohols, have found benzoyl carbinol to be quite effective as a local anesthetic.[12] A series of related studies by Hirschfelder[13] and co-workers has shown the practicability of saligenin as a surgical anesthetic. Very favorable clinical reports have recently been made of this compound.

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[1] *J. Am. Chem. Soc.*, **42** (1920), 1030.

[2] U. S. Patent 1,358,751; *C. A.*, **15** (1921), 412. Clinical report by Bulson in *J. Am. Med. Assoc.*, **1922**, 78, 343.

[3] *Ber.*, **54B** (1921), 2081; *C. A.*, **16** (1922), 1084.

[4] U. S. Patent 1,388,573; *C. A.*, **16** (1922), 990.

[5] *J. Am. Chem. Soc.*, **43** (1921), 1370.

[6] *Ibid.*, **43** (1921), 1320.

[7] *Ber. pharm. Ges.*, **31** (1921), 65; *C. A.*, **15** (1921), 2851.

[8] *C. A.*, **14** (1920), 1595.

[9] U. S. Patent 1,360,994; *C. A.* **15** (1921), 575.

[10] *J. Pharmacol.*, **12** (1918), 263; *C. A.*, **13** (1919), 41.

[11] Nielsen and Higgins, *J. Lab. Clin. Med.*, **7** (1922), 1; Volwiler and Vliet, *J. Am. Chem. Soc.*, **43** (1921), 1672; Schonle and Row, *Ibid.*, **43** (1921), 361.

[12] *Science*, **51** (1920), 497; *C. A.*, **14** (1920), 3476.

[13] *J. Pharmacol.*, **15** (1920), 261; *C. A.*, **15** (1921), 274.

Two products of French origin, stovaine and alypin, have found use in other countries. They may be considered as typical of still another class of local anesthetics. Recent papers on such compounds have been published by Fourneau[14] and by Launoy and Fujimori.[15] Pharmacological tests indicate that the compounds described are of doubtful value.

Two new local anesthetics, the hydrochlorides of nevralteine and its methyl derivative, have been studied by Valenti.[16] They are described as having marked anesthetic properties.

Mention should be made of recent work by Japanese authors. A pharmacological examination by Kubota[17] of allocaine-S, a new local anesthetic, has shown this amino ester to be of limited use. Ogata,[18] in a study of a large number of amines, has shown that both aromatic and aliphatic amines have anesthetic power provided that at least one of seven or more carbon atoms is attached to nitrogen.

With our present knowledge of the relationships between physiological action and chemical constitution, it would be extraordinarily disappointing to some to omit the stereotyped remark that the ideal local anesthetic has not been found. It is quite possible that there is not one ideal local anesthetic; it is more probable that there are several when one considers the different uses to which such compounds are put. With the present state of our knowledge it must be admitted that the modes of attack in the solution of this problem are essentially correct. More rapid and substantial progress would result with a better knowledge of the mechanism of local anesthesia. Furthermore, it must be remembered that as a general rule reactions are inextricably bound up with physicochemical processes—there must be contact before there can be a so-called chemical reaction. Physical chemistry has not as yet rendered full service in this field. The problem, like others related to it, is perhaps as complex as the living body, and advances are dependent not only on the contributions of chemistry, but on those of related fields like pharmacology, surgery, and medicine in general.

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[14] *Bull. soc. chim.*, **29**, 413; *C. A.*, **16** (1921), 3876.

[15] *Compt. rend. soc. biol.*, **82** (1919), 732; *C. A.*, **14** (1920), 3462.

[16] *Arch. farm. sper.*, **25** (1918); *C. A.*, **14** (1920), 775.

[17] *J. Pharm. [illegible]*, **12** (1919), 361; *C. A.*, **13** (1919), 2246.

[18] *J. Pharm. Soc. Jap.*, **456** (1920), 81; *C. A.*, **14** (1919), 3476.

Pharmaceutical Chemistry

By Frank R. Eldred

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THE COMPLEXITY of the problems of life in health and disease is a serious limiting factor in the progress toward more efficient remedial agents. The important advances in this field have usually resulted from the work of many individuals trained not only in chemistry but also in the various branches of biology and medicine. Chemical studies undertaken with no thought of their bearing upon the treatment of disease often supply the foundations for the development of most valuable medicinal products.

Frank R. Eldred

In an attempt to inventory our progress in medicinal chemistry we are confronted by a vast number of individual researches which contribute directly or indirectly to our knowledge of disease and its treatment by chemical agencies. Progress is probably more rapid than at any previous time, owing to the widespread interest in the subject and to the application of newly discovered chemical principles; nevertheless if we had some adequate means for coordinating the work of the army of clinicians, pharmacologists, biologists, and chemists upon whose researches the health and happiness of the human race are so largely dependent, the rate of progress would be increased many fold. Any lack of coördination and coöperation in the attack upon disease constitutes a [illegible].

An example of the time that may elapse between the synthesis of a [illegible] and the discovery of its physiological properties is afforded by the anti-oxime of perillaldehyde, which was prepared in the laboratory of a German chemical plant in 1910 and nine years later was made the subject of a Japanese patent on account of its sweetening power, which is said to be from four to eight times as great as that of saccharin.

It is consequently difficult to evaluate the progress in this field during any definite period or to give credit to those whose work may lead to most important discoveries. In the limits of this brief review no attempt has been made to give complete references or credit for progress to which many workers have contributed.

During the last two years there has been the usual flood of new remedies, but comparatively few of these represent real progress while many of them are distinctly inferior to products already available.

In many instances there is a marked tendency to return to older forms of medication, which have in the meantime been largely replaced by newer remedies or "pure principles." Some of the so-called pure principles fail to represent the activity of the crude product from which they are derived, thus disclosing the need for further knowledge of the chemistry of the parent product as well as of the substances that can be prepared from it. This is especially true of the crude vegetable drugs, since in the preparation of "pure" plant principles physical and chemical changes take place, with the resulting destruction of the original colloidal complexes and accompanying changes in the solubilities of active constituents and their absorption when administered to animals. John Uri Lloyd was a pioneer in pointing out these facts and has made many valuable observations upon the colloidal nature of plant constituents. His original studies, published in the *Proceedings of the American Pharmaceutical Association*, 1876–1889, are very interesting in the light of recent developments.

Digitalis offers an excellent example of the failure to isolate substances which fully represent the physiological activity of the plant. Probably no drug has a more voluminous literature than digitalis, which has been the subject of extensive researches by Schmiedeberg, Kiliani, Cloetta, Kraft, and many others. Cloetta[1] now reports the isolation of pure crystalline digitoxin which differs from any of the previously prepared digitoxins, all of which are considered by Cloetta to be impure mixtures. Pomeroy and Heyl[2] suggest the ready hydrolysis of digitalis principles as an explanation of the varying results obtained in the investigation of the drug, and also call attention to the observation of Tschirch that, while acetone removes the entire activity from digitalis leaf and its aqueous extracts, the acetone extract does not represent the entire activity of the drug. Extraction of an aqueous extract by chloroform resulted in a loss of more than half of the total activity. Tschirch believes that the activity of digitalis is due to the mutual effects of the various glucosides and is not the simple sum of the activity of the individual glucosides. Powdered digitalis leaf and a tincture or infusion prepared from it are probably the best forms for the administration of digitalis, notwithstanding the years of research which have been devoted to this drug. This is also true of many other vegetable drugs which are imperfectly represented by the constituents that have been isolated or from which no active principle has been separated.

Although there is a vast accumulation of data upon the composition of plants, we know very little about the exact physical condition and chemical composition of the substances as they exist in the plant cell before any changes have taken place. The methods which Osborne and his co-workers[3] applied in the investigation of fresh spinach and alfalfa would undoubtedly yield valuable results if employed in the analysis of vegetable drugs.

Cod-liver oil, always popular with the laity, had for a long time been neglected by the medical profession until it was found to be very rich in vitamin-A. Since this discovery was made its use has been constantly increasing and its properties have been generally ascribed to its vitamin content. It has been shown to have a marked effect upon the calcium metabolism, but this property is probably not due to vitamin-A, since cod-liver oil is much more effective than butter fat in preventing rachitic conditions, even when the latter is added to the diet in sufficient quantities to supply much more than the normal requirement of vitamin-A.[4] It has also been reported that cod-liver oil retains its antirachitic properties after the destruction of vitamin-A by exposure to heat and air. It is probable that the physiological effects of cod-liver oil are due in part to its unsaturated fatty acids and its iodine content. It is interesting to note that the American Relief Administration in Russia is supplying cod-liver oil to many day nurseries and children's homes.

Chaulmoogra oil which has been used for many years in the treatment of leprosy with indifferent success has acquired new interest since the preparation of the ethyl esters and sodium salts of the unsaturated acids has made it possible to administer the remedy intramuscularly. Brilliant results are being obtained and the treatment seems to be specific in leprosy.

The administration of substances by inhalation for their systemic effects was suggested by the studies of war gases and in some cases this may prove to be a valuable means of treatment. A rather crude attempt is the proposed treatment of tuberculosis by the inhalation of finely divided calcium carbonate. James Todd[5] has made interesting experiments on the treatment of infected animals by inhalation of ozonized air, and has followed this, with the coöperation of physicians, by the treatment of human cases of tuberculosis and other germ diseases with ozonized oils.

The physiological effects of benzyl alcohol and its esters were studied by Macht who found that they had a relaxing effect on smooth muscle. Together with the known benzyl esters, a number of new benzyl compounds having the typical benzyl effect have been utilized with success in the treatment of many conditions where a sedative action on smooth muscle tissue is desired.

The relative toxicity of a number of alcohols has been determined by Macht,[6] who found an increasing toxicity in the series methyl, ethyl, propyl, butyl, and amyl. The secondary alcohols were less toxic than the corresponding primary alcohols. Kamm[7] tested the normal alcohols on *Paramecia* and reduced his results as well as those of Macht to the numerical expression $1 : 3 : 3^2 : 3^3 : 3^4$--, the molar toxicity of any member of the series being three times that of the preceding member.

Pure isopropyl alcohol is now available in such quantities that it can be used, where applicable, as a substitute for ethyl alcohol. Although more poisonous than ethyl alcohol, it is also more active as an antiseptic and it might therefore replace ethyl alcohol where used for its preservative action.

Denatured alcohol is finding wider use in the manufacture of medicinal products and in the interest of economy its use will no doubt be further extended.

The autoxidation of ethyl ether, with the formation of ether peroxide, hydrogen peroxide, aldehyde, and acetic acid, which is described by Clover,[8] may have an important bearing on its use as an anesthetic. The oxidation is greatly accelerated by light.

A number of dyes, particularly the acridine dyes, find a continually increasing use as antiseptics. Further studies in the acridine series have led to the preparation of 2-ethoxy-6,9-diaminoacridine, which is said to be superior to the acridine compounds now in use. A number of other dyes have been found to be active germicides. Mercurochrome, dibromo-oxymercury-fluorescein, seems to be a very useful urinary antiseptic and Hirschfelder[9] has found the mercury compounds of saligenin and of *p*-hydroxy-*m*-nitrophenyl carbinol to be effective as antiseptics. Johnson and Lane[10] have prepared several new derivatives of resorcinol, and have found that the phenol coefficients of the series, *viz.*, resorcinol, ethyl resorcinol, *n*-propyl resorcinol, *n*-butyl resorcinol, increase in the following order 0.3, 1.5, 4.3, 8.0. This observation will be of value in future work on antiseptics. The comparative toxicity of germicides to bacteria of different species, or even different strains, is not constant. The application of this "specificity of disinfectants" to the practical testing and use of germicides was first emphasized by Walters.[11] It has been found that even the various chlorine disinfectants differ greatly in their relative toxicity to various organisms. Attention is called to the efficiency of steam-distilled pine oil in killing *B. typhosus* and the high resistance of *M. aureus* and *B. anthracis* to this agent.[12]

Cymene and piperitone, a constituent of certain eucalyptus oils, may serve as sources for the commercial production of thymol, one of the valuable remedies in hookworm infections. Carvacrol has been found to be fully as effective as thymol, and since it can be readily prepared from cymene, it should find extensive use. Chloroform and carbon tetrachloride have also been successfully used in hookworm infection.

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[1] *J. Chem. Soc.*, **120**, 1 (1921), 39.

[2] *Am. J. Pharm.*, **92** (1920), 394.

[3] *J. Biol. Chem.*, **42** (1920), 1; **49** (1921), 63.

[4] *Ibid.*, **50** (1922), 5.

[5] "Experiments with Oxygen in Disease," Pittsburgh, Pa., 1921.

[6] *C. A.*, **15** (1921), 122.

[7] *Science*, **54** (1921), 55.

[8] *J. Am. Chem. Soc.*, **44** (1922), 1107.

[9] *Ibid.*, **42** (1920), 2678.

[10] *Ibid.*, **43** (1921), 348.

[11] *Am. J. Pub. Health*, **7** (1917), 1030.

[12] *U. S. Dept. Agr., Bur. Chem., Bull.* **989** (1921), 11.

Cinchophen continues to increase in popularity and a number of closely related compounds have been placed on the market. Bogert and Abrahamson[13] suggest that a new thiazole derivative which they have prepared, 2-phenylbenzothiazole-6-carboxylic acid, may, from its analogy to cinchophen, have similar physiological properties.

A number of new barbituric acid derivatives have been prepared and some of them have been placed on the market, but barbital seems to be fully as efficient as any of the newer derivatives. Luminal has been found particularly valuable in epilepsy.

The organic arsenic derivatives are the subject of much important research. Arsphenamine and neoarsphenamine remain as the most valuable remedies in syphilis, although promising results have been attained with some of the newer compounds. Much progress has been made in the methods of manufacturing and testing arsphenamine and neoarsphenamine, and products less toxic than the original imported products are now available. Stieglitz and co-workers[14] have prepared 5,5′-mercuri-bis-3-nitro-4-hydroxyphenylarsonic acid and are continuing the investigation with the object of producing a compound for therapeutic use containing both arsenic and mercury.

Bismuth, administered intramuscularly, in the form of potassium and sodium tartrobismuthate suspended in oil or bismuth and ammonium citrate in aqueous solution, is reported to act as a specific in syphilis.

Extensive researches have been devoted to the cinchona alkaloids. Jacobs and Heidelberger have prepared many new derivatives in the cinchona series with the object of finding compounds that will have a specific action in pneumonia. Through the studies of Bass, the quinine treatment of malaria has become much more effective, but it is not improbable that some new derivative of the cinchona alkaloids will be found which will be even more efficient than quinine. An alkaloidal product from *Lobelia inflata* prepared by a patented process is now on the market. Wieland,[15] who studied the alkaloids of lobelia, isolated two crystalline alkaloids, lobeline and lobelidine. These alkaloids will probably be useful therapeutic agents. Cushny has made the interesting observation that *l*-hyoscine is 15 to 18 times as active as *d*-hyoscine as a mydriatic, but that the two forms are identical in their action on the central nervous system and therefore in their production of "twilight sleep."

Karrer[16] and co-workers have prepared a number of new amino alcohols and cholines, some of which have an action on the uterus similar to that of ergot. Shepherd's-purse (*Capsella bursa-pastoris*), which was used during the war as a substitute for ergot, has been found to contain choline and acetylcholine; the presence of tyramine is regarded as probable and that of histamine doubtful.

The manufacture of digestive enzymes from animal sources has been carried on chiefly for medicinal preparations but they are now being used in increasing quantities in the food, leather, and textile industries.

The use of gland extracts in medicine is rapidly increasing and valuable contributions are being made to our knowledge of the composition of these extracts. Notable among such studies is the work of Kendall on thyroxin, the active substance of the thyroid gland. A concentrated preparation of the internal secretion of the pancreas is said to have been used with remarkable success in cases of diabetes. The active principles of the pituitary have not yet been determined, although much progress has been made by Abel, Dale, Dudley, and others. Drummond and Cannan[17] state that tethelin is an impure mixture of lipoids, and that the anterior lobe of the pituitary does not seem to influence growth. Ovarian and placental extracts have been found very useful in disturbances of menstruation and pregnancy.

Vitamins are to be considered from the standpoint of foods, as cod-liver oil and certain yeast preparations are the only useful vitamin-containing products that can be classed as medicines. It is possible that with further knowledge of the functions of vitamins and their separation from plant and animal products, vitamin preparations will become valuable as medicines.

McClendon[18] has suggested that our use of refined table salt is a mistake, and that it might be well to substitute a sterilized sea salt which would supply not only iodine, but also numerous other elements which may be deficient in the diet.

The relation of calcium metabolism to rickets has been the subject of much study. Sunlight has been found to have an effect similar to that of cod-liver oil on rachitic animals. Mason states that calcium chloride is better absorbed than calcium lactate and it is interesting to note that a single dose of cod-liver oil administered with the lactate seemed to increase the absorption of calcium.

Colloidal metals have been used, in many cases with apparent success, in combating various infections. Colloidal antimony is reported as being very efficacious in the treatment of leprosy.

Corresponding to the toxic relations between arsenic and arsenious acids, the ions of selenious and tellurious acids have been found to be much more effective in killing bacteria than the ions of selenic and telluric acids. Germanium dioxide has been found to stimulate the formation of red blood-cells.

Viewing the manufacture of medicinal products from an industrial standpoint, small-scale operations are the rule and engineering and factory practice is frequently not up to the standard required for larger operations. Much can be gained by a careful study of the methods employed in other branches of chemical industry where success is dependent upon progress in engineering and upon economical management.

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[13] *J. Am.* [illegible] 44 [illegible]

[14] [illegible] 43 [illegible]

[15] *Ber.* 54 [illegible]

[16] *J. Chem.* [illegible] 120, [illegible]

[17] *C. A.*, **16** (1922), 1974.

[18] *Science*, **55** (1922), 358.

Final arrangements have now been completed for the sulfur investigations to be administered by the Crop Protection Institute, utilizing funds supplied by the Union Sulphur Co., the Freeport Sulphur Co., and the Texas Gulf Sulphur Company. The phytopathological phase of the work will be carried out by Mr. H. C. Young at the Missouri Botanical Garden, St. Louis, under the direction of Dr. B. M. Duggar. Approach to this phase of the project will be along the line of the fundamental effects of temperature, moisture, and other conditions on the fungicidal action of sulfur. The entomological phase of the investigation will be conducted at the Geneva, N. Y., Experiment Station and in part at Ohio State University, by Mr. F. H. Lathrop, under the direction of Prof. P. J. Parrott and Dr. Herbert Osborn. Each phase of the project will run for two years, during which time it is expected that substantial progress will be made and real contributions to the knowledge and use of sulfur will be achieved.

After constituting for almost four years a division of the Czechoslovak Federation of the Chemical Industry, the dyestuffs-producing interests of Czechoslovakia have become associated in an independent federation, to be allied with the Federation of Czechoslovak Industrialists. This separate organization was considered necessary for closer unity with respect to customs needs and the operation of the commercial agreement with Germany. The federation comprises seven sections divided according to nature and use of products.

Chemistry as an Aid to the Tobacco Industry

By A. L. Chesley

Chemist, The American Tobacco Co., New York, N. Y.

IT IS OFTEN asked, "What need has the tobacco industry for a chemist?" Every process, every treatment that tobacco undergoes, from the time the seed is planted until the cured and aged tobacco is ready for the consumer, is based on chemical reactions and changes. A few of these are understood, but in most cases neither the cause nor effect is known. For instance, what causes Turkish tobacco grown in Turkey to have an entirely different aroma from tobacco grown in the same way and from the same seed in California? Why will not plants grown in Cuba, and transplanted into Florida with Cuban soil around the roots, mature into the same quality of leaf as if they had matured in Cuba? Why are Sumatra wrappers grown in Florida thicker and heavier bodied than those grown in Sumatra? Could these questions be answered it would be a great boon to the tobacco industry; but because tobacco is such a complex product of nature, and so many things, such as color, aroma, burning properties, body, toughness, and pliability, have a direct bearing on the quality of the leaf and the sale of the manufactured article, chemists have not been able to make the great strides in aiding, controlling, and improving the various primary processes that they have in other industries. The main reason for this is because the intricate chemical reactions carried on by the plant are but little understood, and there are many variables to contend with.

A. L. Chesley

Tobacco Growers' Problems

But let us see what the chemist has accomplished. If we take up the primary processes, we find many instances where he has been of great aid to progress in this industry. His knowledge was needed in solving the fertilizer problem. The ratio of ammonia, phosphoric acid, and potash in the fertilizer is of great importance and must be controlled to suit the type of tobacco raised far more closely than in growing most crops. Too much plant food is as injurious as too little. Lack of ammonia causes the growth to be backward, and to obtain a good quality the growth must be rapid and uninterrupted. Too much ammonia makes it very strong, dark in color, and increases the nicotine content. A fertilizer deficient in potash or containing chlorides will cause the tobacco to be of poor burning quality. While an excess of sulfates is harmful, they are not as injurious as chlorides. A large cigar company has just issued instructions to its representatives in Porto Rico to reduce the amount of ammonia in the fertilizer in order to obtain leaf of lighter color. The custom was to use lime with the fertilizer to improve the burning quality. It was found, however, that alkaline materials create conditions favorable to certain fungus diseases, especially root rot. To-day this class of materials is not used except when it is impossible to obtain the desired quality in any other way. The source of the fertilizer has a great deal to do with the various qualities of the leaf. Stable manure, for instance, should not be used where a very light color is desired; it also increases the chlorine content of the leaf.

After the "topping" process, which means the cutting off of the flower bud, the leaves become thicker, heavier, brittle, and begin to droop. This is also a sign of maturity. The reason for it has been shown to be that the plant food which ordinarily would be carried into the flower and seeds is forced into the leaf. Thus chemistry has explained why "topping" produces a larger and better bodied leaf than by allowing the plant to pursue its natural course.

In the curing of most plants, the only object is to bring about such a condition that the material can be stored until the next crop without deteriorating. In the curing of tobacco, besides the storage qualities, there are more important objects to be attained, production of a good aroma and light color, fixing the color, and securing a tough and supple leaf. Curing was formerly accomplished by building a fire underneath the leaves and allowing the smoke to escape through them. To-day only export tobacco is cured in this manner. Tobacco for home consumption is cured by evaporating the moisture in the plant juices in such a manner that the life processes of the plant will continue to function until certain food materials have been consumed and other compounds produced in their place. In some methods of curing the sugars remain and in others they disappear; citric, malic, and oxalic acids are produced from the sugars; later these are changed to a large extent into carbon dioxide and water; citric acid is not as readily oxidized during this change as the other two. In another method the acetic acid increases six times and the nitric acid decreases one-half. In another there is a transmigration of the salts through the veins to the midrib and into the stalk.

You have often seen a cigarette sputter while held in the hand, and have probably thought it due to added potassium nitrate. This is not so, but is due to a crystal of potassium nitrate which occurs naturally in the tobacco. As much as 2 per cent of potassium nitrate is found along the midrib. Years ago it was the custom to add potassium nitrate to improve leaf of poor burning quality. To-day this is made unnecessary by the use of proper fertilizers and control of the growth and curing of the leaf.

While many of the changes that take place are known, it has not been possible to induce them by artificial means or even to shorten the time necessary for them to take place. Several processes have been patented, for which startling claims have been made, but they have proved to be of no value. As a rule they only injured the tobacco so it was not suitable for use.

It has been possible to aid by controlling the temperature and humidity so that those conditions which best suit the production of these changes may be obtained under adverse climatic conditions. To-day all large growers have modern curing barns so they can keep the temperature in the barn slightly higher than the outside temperature, thus increasing the moisture absorptive power of the air. On the other hand, as the changes during curing are chemical, the air must not have too great a drying power or the changes will not take place.

PROTECTION OF BRANDS

The chemist in the tobacco industry is concerned with everything entering into the manufacture of the various brands and the placing of them upon the market, but the tobacco itself. The main assets of a tobacco concern are its brands; therefore, one of his chief duties is to keep up the standard of those brands. There is probably nothing in which slight changes are so noticeable as in tobacco smoke. The manufacturer has learned by experience, and often to the detriment of his profits, that he must keep his brands uniform in every way from day to day, and it is along this line that the chemist is of the greatest value. It is here where the greatest progress has been made.

Many supplies are peculiar to the industry itself. For some of them no standards had been set. Even the suppliers, in some instances, had no knowledge of the quality of their products. To-day, in our company, every supply must first pass the test of quality before it can be purchased. Even the suppliers themselves have to a certain extent been investigated. Preference is often given to the one who has proved that his quality can always be depended upon, even when his price is slightly higher and another's sample analyzes equally as good. Thus, after the first few years, supplies below standard decreased; so that one year but 30 samples were received that were below requirements, and most of these were rejected before purchase. Suppliers learned that the quality of their goods was being watched and took care to see that their goods met our specifications. Since the war there has been quite an increase due principally to competition and to stocks bought for speculation.

FADING OF LITHOGRAPHS

Probably the largest single piece of research undertaken during the last two years was on the fading of lithographs. At the time the matter was agitated it caused quite a furor among ink manufacturers. They claimed there was no need of it, that their inks were permanent and they would guarantee them. They would not, however, back their guarantee with cold cash, using the argument that they did not have control of the paste, or that the posters might be exposed where fumes would cause fading. A concern had suffered because of the fading quality of the ink used on its lithographs. It received reimbursement for the posters but not for the posting. A national posting is for 30 days and costs about $275,000, the posters costing about $25,000. Obtaining reimbursement for the cost of the posters is not much satisfaction when the entire outlay is considered. As no concern would guarantee us against this loss, it became necessary to find some way to protect ourselves. We made over 1000 tests on a billboard through the months of June, July, and August, with inks of known composition, and compared the results with tests made on the Fade-O-Meter. As the humidity and temperature around New York City is the most trying on lithograph inks, it was only necessary to find the equivalent for this section in order to protect ourselves all over the United States. It was found that 50 hrs. on the Fade-O-Meter were equivalent to 30 days on a billboard having a southern exposure for these months in this vicinity, and would protect us in practically every instance. It was also found in these tests that a color would have different fading qualities according to the other ingredients used with it, and that some supposedly fast inks would fade. The Fade-O-Meter Company has since published results showing that 40 hrs. are equivalent to 30 days' posting in Chicago.

CIGARETTE PAPER

Outside of tobacco, the most important article used in cigarette manufacture is the paper. It must be odorless, tasteless, of sufficient opaqueness, and burn evenly with the tobacco. This paper, except a small quantity used for special purposes, is made of pure linen stock and an inert filler, calcium carbonate. The latter is necessary to give the necessary whiteness to the paper, prevent air being drawn through it, and make it burn readily. During the war there was a great deal of trouble with poor burning paper. Very often cigarettes which would not stay lighted would be found on the market. The trouble was found to be in the purity of the filler. It really should not be called an impurity as it had always been allowed, and some manufacturers claimed it to be beneficial. It was found, however, that in the amounts in which it was occurring it had a fireproofing action which varied according to the type of tobacco in the cigarette. Tests were immediately made in all factories on every reel of paper. One factory alone rejected 1000 reels, which would have made 40,000,000 cigarettes. The effect on the brands of this large amount of bad burning cigarettes can be imagined.

At about the same time cigarettes having a foreign odor appeared on the market. This odor was also located in the paper, and tests were installed in the factories to prevent any such paper being used. The cause was not determined until some time later when it was traced to the bleach used in the cleaning of the linen stock. Almost all cigarette paper comes from France, and the manufacturer, because of war conditions, had to find a new supply of bleach. This he obtained from Switzerland where spring water was used in its manufacture. This water contained a trace of iodine compounds which caused the trouble. It was not possible to get an iodine reaction in the paper itself, the quantity present was so slight, yet the odor was noticeable in the smoke.

In times past, manufacturers of cigarette paper, it is said, have used potassium nitrate to aid the burning quality. This is absolutely unnecessary when the paper is properly manufactured, and the right quality of stock is used. A cigarette paper containing potassium nitrate indicates that the manufacturer does not know how to control his process or he is trying to cover up a case of poor manufacture. It is useless to test paper which has been taken from cigarettes for nitrates, as nitrates occur naturally in tobacco and the paper often absorbs a sufficient quantity to give the reaction. Because of these war troubles a great deal of work was done, and is still being done, on cigarette paper. As a result there are but one or two manufacturers who make a paper considered satisfactory for our use. Some time ago, a manufacturer wrote that he was glad he had at last got the quality of his paper so that it satisfied the chemical department.

ADHESIVES

The matter of adhesives is a very important one with a tobacco concern, as they have to be of many qualities and kinds. Each purpose and each type of machine require an adhesive of special properties. Two of the most important properties are that they shall be odorless and transparent. A short time ago the concern furnishing paste used in cork-tipping cigarettes went out of business. No other concern was making this paste as this concern had developed it for this special purpose. This paste had already been analyzed and by modifying a paste used for another purpose our needs were immediately met. In another instance the revenue stamps were not adhering properly to the cigarette shells. It was found that because of the printing ink used, the paste did not contain enough water to penetrate the surface of the shell before it had dried. For sealing shipping containers, research was carried out on various grades of sodium silicate on the market. It was found we could get a better bond, increase the speed of the men, and use less silicate by getting the right kind. In some instances there was a difference of 50 per cent in the number of containers sealed by two different silicates. When the last railroad strike occurred, a supply of paste for use in attaching labels at one of our southern factories was delayed. The lack of this paste meant shutting down the entire factory. A formula had previously been worked out for a similar paste, but it was not being used. This factory was able to run the entire time by getting in its raw materials by parcel post and making its own paste. While the actual value of this cannot be figured in dollars and cents, the loss a shutdown would have entailed will probably cover the cost of the department for some time. This factory is now making its own paste at a saving of about $7500 a year. The savings on adhesives alone since the chemical department has been in existence, figured on an accumulative basis, are approximately $75,000.

In order to better protect cigarettes from drying out, a layer of paraffin was used for pasting the paper to the tinfoil. During the summer months complaints were received about cigarettes being stained. It was found that although the melting point of the paraffin was 130° F., if kept at 119° F., it would become fluid enough to soak through the paper. Furthermore, a container placed in the sun would absorb sufficient heat, so that, with a temperature of 89° F. in the open air, the temperature in the container reached 122° F. It was further found that in a mixture of two paraffins of different melting points, the staining point was about six degrees below the lower melting point.

CONTROL OF MOISTURE CONTENT

Up to two years ago we were receiving a material which varied very greatly in the amount of moisture it contained, mechanical impurities, and condition in which it was received. As a result there was a loss of 15 to 20 per cent on all that was bought. The handling of the material was costly. It was very hard to tell whether we were using the same quantity each time or not, and getting the material out of the containers was difficult. Often it would be fermented and have to be thrown away or would have a scorched taste because the evaporation had not been properly controlled. It was claimed that we could not obtain this material in any other way, inasmuch as it would be impossible to educate the producers, who are mostly small farmers. This material is maple sugar, many pounds of which are used each year by the tobacco industry. Our present specifications call for it to be put up in boxes of 60 lbs. each, lined with paraffined paper, to contain not over 7 per cent of moisture and not more than 6 per cent of invert sugar. The amount of invert sugar is a guide as to what temperature the evaporation has been carried, and as to whether the sap used was fresh or fermented. To be sure, we have to pay a higher price but the quality is worth the increased cost.

Few materials are so affected by changes of humidity as tobacco. It will take up or give off moisture very readily. The writer has found that if conditions are favorable, tobacco will take on moisture until it contains as much as 30 per cent. Being high in nitrogenous matters, when the moisture content becomes too high it is apt to mold. It is therefore necessary for tobacco concerns to manufacture their goods under absolutely sanitary conditions to prevent a very large loss in returned goods. It has been found necessary in one or two instances, especially in cigar factories, to close the factory and fumigate with formaldehyde to get rid of the mold spores. To-day probably 99 per cent of the tobacco which becomes moldy is through no fault of manufacture, but because of the conditions in small retail stores. Yet, the manufacturer, in order to protect his brands, must keep moldy goods off the market and suffer the loss for which he is not to blame. He has, however, made wonderful progress in this respect, when it is considered that the state of Texas probably accounts for 25 per cent of the moldy tobacco of the whole United States and the states bordering the Gulf of Mexico account for 75 per cent. Last fall the writer saw a box of tobacco manufactured in 1908, and although this had been in a retail dealer's store for twelve years the tobacco was in excellent condition. During the first three months of this year, cigarettes manufactured during 1921 showed but one moldy out of every 140,000 manufactured. When it is considered that some of these had been on the market for fourteen months, the extreme care used in manufacture and packing is evident. The manufacturer who does not understand thoroughly the necessity of the utmost cleanliness in his plants will find himself in all kinds of trouble.

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During the war we were shut off from the source of supply of a very important material. A similar product was native to America but had never been gathered. On testing out the American variety it was found to be perfectly suitable, and, if anything, better suited to our needs. Up to the present time we have been able to obtain all we need from American sources, and unless something unforeseen happens shall not return to the use of the foreign variety.

Thus the chemist has his place in the tobacco industry, and has assisted in its forward progress the same as he has elsewhere. Although he is not yet able to be of the assistance he would like to be in the maturing, curing, aging, and preparation of tobacco for the machines, because of his limited understanding of plant processes, there are problems arising every day where his services are of value. He cannot introduce the characteristics of one tobacco into another, make good burning tobacco out of poor, or light colored out of dark, for the reason that it is impossible to dissolve out one substance without removing others which are necessary, and he cannot add something to tobacco in the same way that nature does. The chemist has been of great assistance to the farmer in the control of his soil, fertilizer, and insect pests, and rotation of his crops to obtain the greatest yield. But if a manufacturer wants more Turkish he must import more; Virginia tobacco cannot be changed into Burley, or Burley into Perique. If a mellow tobacco is wanted it must age for from two to three years. Perhaps in the future the chemists will solve these problems.

Royalties received from the production of minerals on leased public lands are becoming quite an important item of Federal revenue. The Bureau of Mines reports receipts totaling $5,766,507 to June 30, 1922, from the production of oil, gas, and gasoline in the states of Wyoming, Montana, and California. Oil and gas royalties are now being reported in excess of half a million dollars per month, receipts for June 1922 amounting to $565,199. Royalties from the production of oil, amounting to $550,708, constitute the bulk of the June 1922 receipts. Royalties on gas amounted to $11,719, and on a natural-gas gasoline were $2771.

Reports made to the United States Bureau of Mines by all manufacturers of permissible explosives covering the year 1921 show that 93.5 per cent of such explosives sold during that year belong to the ammonium nitrate class. The total quantity of commercial ammonium nitrate used in permissible explosives during 1921 aggregated 25,381,500 lbs. The total quantity of nitroglycerin and "modified" nitroglycerin used in permissible explosives aggregated 3,974,000 lbs., for the manufacture of which approximately 1,766,000 lbs. of glycerol were used. By "modified" nitroglycerin is meant the products obtained by the nitration of a mixture of glycerol and certain compounds.

Recent Contributions of Chemistry to Photography

By S. E. Sheppard

Eastman Kodak Co., Rochester, N. Y.

Advance in photography in the last two years has not been marked by radical innovations such as new processes, but rather by a deepening of knowledge of fundamental processes and the opening up of new points of view. At the same time the sum of progress in all directions, theoretical and applied, has been considerable. The reviewer has had to condense this article from a preliminary survey of some four times its present magnitude, and even then scant justice was done to the more important subjects. The present review is, therefore, selective; many interesting items must pass unnoticed, and others be only imperfectly documented.

S. E. Sheppard

Support or Base for Sensitive Coatings

Many new compositions of cellulose, and of its nitrates and acetates, have been patented, as well as new methods of manufacture of the acetates. The number of commercially available solvents appears to be increasing, and in this connection the hydrogenation derivatives of benzene and naphthalene show promise.

Gelatin and Emulsifying Media

During the past two years contributions of physical chemistry to the technology of gelatin and glue have continued. The writer has dealt recently with the role of gelatin in the photographic process,[1,*] and a brief account must suffice. The function of gelatin in photography has two main aspects: first, in emulsion making; second, as a colloid vehicle of the developable, developing, and developed image. Of the former, the statement of B. V. Storr[2] on the insufficiency of the physical properties as guides to the suitability of gelatins for emulsions and the relative unimportance of the more obvious chemical properties holds true. In this connection a paper by F. L. Seymour-Jones[3] on the "Chemical Constituents of Skin" deserves note as a compact and up-to-date account of the proteins and albuminoids of hide substance.

On the second count, progress has been steady. H. R. Procter's theory of swelling[4] as a function of chemical combination has been mathematically and experimentally confirmed by J. A. Wilson[5] and by J. Loeb.[6] The last named has cogently demonstrated the unique importance of the hydrogen-ion concentration for all primary physical and chemical reactions of the ampholyte, gelatin. Donnan's membrane equilibrium and the determination of pH are [illegible] fundamental importance for photographic processes as for tanning. The depressing action of neutral salts on swelling in presence of alkaline developers is in agreement with this result.[7]

[illegible] part remains for the sus[illegible] after treatment of gelatin with dehydrating and tanning agents. The important contributions of R. H. Bogue,[8] C. R. Smith,[9] and H. Oakes[10] to the structure theory of gelatin solutions and jellies demand notice in this same connection, as also the development of more precise methods of measurement of such properties as "jelly strength" (elasticity), "setting point," viscosity, etc.[11] Moreover, from the photographic standpoint, the nonisotropic character of the swelling and drying of gelatin jellies is of considerable importance, and the writer and F. A. Elliott[12] have suggested that this and certain hysteresis factors can be explained without internal structure theories.

While nothing has yet displaced gelatin as general carrier for sensitive salts, mention may be made of J. Rheinberger's[13] work on modifications of collodion, and on the Cellophane Company's[14] processes for utilizing viscose cellulose as carrier of silver halides, generally formed by impregnation.

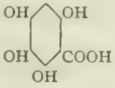
Negative Emulsions, and the Latent Image

With respect to fundamental negative material of photography, the gelatino-silver bromide emulsion, no small progress is to be recorded. It was known that in coarser grained emulsions the grains were crystalline, and investigations in the Research Laboratory of the Eastman Kodak Company[15] have shown that the crystals are entirely of the regular system, and the diakisdo-decahedral class. This remains true for solid (homogeneous) solutions of bromide and iodide. Wilsey[16] has shown that the effect of the iodide is to change the lattice spacing somewhat, also that the grains of the finest colloid emulsions are crystalline, of the same system. The suggestion of Trivelli and Sheppard[17] that "silver iodide acts as a crystallization buffer substance* * * * restricting increase in size of grain" was confirmed by C. A. Schleussner and H. Beck[18] in a study of primary gelatino-iodo-bromide emulsions. Precipitation of iodide with bromide lessens the crystallization of the grains. They also note that the optimum iodide content depends upon the emulsification process, and lies between 1 and 5 per cent. An interesting optical sensitizing effect for red light by iodide (and cyanide), discovered by F. F. Renwick,[19] has been shown by Sheppard[20] to be specific to certain emulsions. While Renwick attributes it to a direct coagulating effect on silver amicrons already present, Sheppard suggests that it is due to an orienting effect of iodide on colloid silver formed by exposure itself. The panchromatic sensitizing by bathing plates in bisulfite followed by alkaline washing, observed by Capstaff and Bullock,[21] is also attributed to optical sensitizing by colloid silver, in line with Lüppo-Cramer's original discovery.

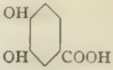
The distribution of sizes of grain in an emulsion as affecting its photographic properties, attention to which was first directed by Mees, has become the subject of important work. R. Slade and G. I. Higson[22] broke ground in this direction, correlating the steep gradation of "photomechanical process" plates with uniformity of grain size. This has been questioned by Renwick,[23] but seems to have a limited validity, provided the sensitivity distribution follows the size. The general question of the relation of sensitivity of grains to their size has been brought to the fore by The. Svedberg[24] and collaborators. This well-known colloid chemist introduced a very valuable method of grain analysis; preparing a one-grain layer, in a manner similar to that of other workers, after definite exposure steps and development he removed the developed silver grain with a silver solvent. He was thus able to determine by difference counts and size measurements the grains made developable by light (and other agencies, as X-rays, α-rays, hydrogen peroxide) and found not only that grains of the same size might have different sensitivity, but also that within the same emulsion the sensitivity increased with size of grain. The size-classification methods used by Svedberg were comparatively rough. More precise and closer methods have been developed and used by E. P. Wightman and S. E. Sheppard,[25] and by Wightman, Trivelli, and Sheppard,[26] by which the size-frequency curves of a large number of emulsions of widely differing "speeds," etc., have been measured. These results show again a very general correlation of "speed" with grain size. In their work Svedberg and Anderson found in the case of α-rays that the projective area of a grain determined its chance of being hit, and referred to the possibility that exposure to light might follow a similar law, if light had a discrete nature, as suggested by Einstein and J. J. Thomson. A "normal" law of exposure, based on such a hypothesis, had already been suggested by Ross;[27] the hypothesis was mathematically developed by L. Silberstein[28] on the assumptions (*a*) that a grain becomes developable when fully hit by one quantum, and (*b*) that the chance of being hit is proportional to the projective area of a grain or contiguous clump of grains. Silberstein's formula found close experimental confirmation by A. P. H. Trivelli and F. L. Righter[29] using Svedberg's procedure. This result raises the issue, whether the variable "sensitivity" of grains of the same emulsion is purely a question of projective area and quantum encounter, or whether inherent sensitivity differences exist; such differences are feasible on the hypothesis that the grains contain reduction nuclei, *e. g.*, the "Reifungs-Keime" suggested by J. M. Edér, and by the existence of which Lüppo-Cramer[30] has interpreted many interesting observations. In fact, in the second Hurter and Driffield Memorial Lecture, F. F. Renwick,[31] after ably marshaling the strong evidence that the latent image consists of colloid silver dispersed in silver halide, suggested that its formation, at any rate in "high speed" plates, is due, not to photochemical decomposition of silver halide, but solely to a photoelectric coagulation of silver amicrons to neutral particles capable of acting as nuclei in development. This view has been criticized,[32] but there exists considerable evidence for a primary role of sensitizing nuclei.[33] The issue has been more sharply defined by very recent work of Svedberg.[34] He has refined his method of grain analysis by utilizing M. B. Hodgson's[35] observation that on early interruption of development of a single grain layer, development is found to have commenced at one or more centers in the grain. Svedberg assumes that these centers are distributed according to the laws of chance, and a grain becomes developable if possessing one or more of a certain size. The probability expression derived for relation to size of grain and chance of developability agreed with observations for two size-classes of grains exposed to light and X-rays. The outcome of work in this direction is of capital importance, not only for the theory of photographic emulsions, but for radiation theory.

DEVELOPERS AND DEVELOPMENT

The gamut of photographic possibilities is fairly well covered by existing developing agents. Hence the introduction of new ones, if photographically adequate, is likely to depend mainly on production cost. *p*-Amino-carvacrol, derived from *p*-cymene,[36] a by-product of the pulp industry, has not come into use. "Neol" (*p*-amino-salicylic acid) introduced by Hauff & Company with the usual claims of abnormal capabilities,[37] has been found[38] to belong to the "slow" group, like hydroquinone. A useful review of organic developers has been made by A. and L. Lumière and A. Seyewetz.[39] These authors also[40] find that the reported developing properties of the leuco-bases of rosaniline dyes[41] were probably due to impurities. The question of constitution has been further discussed by B. Homolka,[42] who concludes that the failure of gallic acid and protocatechuic acid to develop is due to anhydride condensation between the COOH and a para-OH group; if prevented, such substances develop. The possibility of more accurately relating constitution to developing power (as reduction potential) is increased by A. Nietz'[43] work on the physical chemistry of development, particularly by his improvement of Sheppard's method of determining reduction potentials by bromide depression of density. The formation of an initial adsorption compound of developer and silver halide is suggested and experimentally supported by Sheppard and Meyer.[44] Such adsorption effects, including both displacement of one adsorbent by another, and incipient peptization, probably play a large part in the effects observed by Lüppo-Cramer[45] of dyes in development. These included accelerating, restraining, and fogging effects. A. Steigman[46] has brought out interesting results, bearing on the difference between physical and chemical development, in his studies in the reduction of silver solutions by sodium hyposulfite.



Gallic acid



Protocatechuic acid

In relation to manufacture, a process assigned to The Barrett Company[47] for the catalytic oxidation of benzene to quinone is of interest, and one of F. F. Kitchin[48] for the electrolytic oxidation of benzene in 10 per cent sulfuric acid to quinone, while the electrolytic manufacture of *p*-amino-phenol[49] has been described by A. S. MacDaniel and collaborators.

DESENSITIZING AND DESENSITIZERS

Logically this should be discussed in connection with emulsions and the latent image. Practically, Lüppo-Cramer's noteworthy discoveries have joined it up with development. Following up his observations on the desensitizing action of organic developers, notably amidol, he found this due to their oxidation products.[50] This led him to search for dyes that might, in small quantities, act as desensitizers in development. In phenosafranine[51] he found a desensitizer, such that pre-treatment for 1 min. in a 1:2000 solution allowed an exposed plate to be developed in strong yellow light; by addition to the developer white light could be used.[52] In many cases, however, the alkalinity of the developer precipitates the free dye base. Besides dyes of the safranine class, Methylene Blue, Auramine O, and Brilliant Green were found effective, but liable to fog. This fogging appears to be general for basic dyes, but may be neutralized by acid dyes, such as Erythrosine, without destroying the desensitizing effect. In a later paper, Lüppo-Cramer[53] concludes that this type of desensitizing is an oxidation process, affecting the nascent latent image. The apparent improbability of an oxidation process occurring in the presence of developers of high reduction potential is met by A. Steigman[54] with the suggestion that the desensitizer is adsorbed strongly compared with the developer.

FIXING AND HARDENING

The physical chemistry of the acid-fixing bath in relation to gelatin has been investigated by Sheppard and collaborators.[55] The reinforcement of the action of formalin by salts such as sodium sulfate, for hardening prior to development has been patented in England.[56] In the recovery of silver from waste "hypo" the zinc dust method has been considerably used,[57] and A. Steigman[58] has proposed the use of sodium hyposulfite.

INTENSIFICATION AND REDUCTION

Besides the application of various toning processes to intensification, the only noteworthy item is the modification of Lumière and Seyewetz[59] of the chromium intensification process by the use of salts of chlorochromic acid. These authors also discuss the use of *p*-quinone[60] in intensification, bleaching, and reduction. The chemistry of persulfate reduction has received considerable attention. The importance of acidity was brought out by Lumière and Seyewetz[61] while S. E. Sheppard (with A. Ballard)[62] and G. I. Higson[63] have shown that silver ions catalyze the decomposition of persulfate in the reaction $S_2O_8'' + H_2O \longrightarrow 2HSO_4' + O$.

POSITIVE PROCESSES

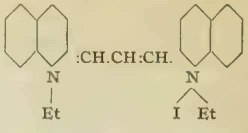
F. Weigert's work on print-out processes has been noted. The photochemistry of thallous chloride is discussed by C. Renz.[64] J. M. Eder[65] has used the light sensitiveness of leuco-bases of dyes in collodion for actinometry. Donisthorpe's dye-impression process, for making color prints on paper or other gelatin coated base by imbibition from a differentially dyed negative, has been further developed.[66] A dye printing process of the Badische Company is discussed by Eder.[67] F. Formstecher[68] has given a good account of the theory of the print-out process in relation of tone to subdivision, while R. Schwarz and H. Stock[69] found that the release of bromine from exposed silver bromide approximately paralleled the photographic blackening.

TONING

The most important advance in toning processes is dye mordanting. In this, the silver image is converted either into an insoluble silver compound mordanting dye, as in Traube's diachrome process with silver iodide, or eventually into other insoluble inorganic compounds capable of mordanting. J. M. Blaney[70] has patented conversion of the image to stannic ferrocyanide; F. E. Ives[71] bleaches the image with potassium ferrocyanide and chromic acid to mordant basic dyes; a copper salt is proposed by J. H. Christensen,[72] and in a British patent A. Traube[73] describes general methods for production of double salts of copper, uranium, iron, etc., to be dyed with basic dyes. The use of iron toned images for mordanting dyes was patented by J. I. Crabtree.[74]

COLOR SENSITIZING

Apart from dye toning, the chief contribution of chemistry to color photography is in dyes for optical sensitizing and selective screening. The impulse given by the war to investigation and production of such dyes in America, Britain, and France has been continued. The isocyanines, resulting from the condensation of quinoline alkiodides or quinaldine alkiodides by alkaline hydroxides, have been investigated very fully by W. J. Pope and W. H. Mills,[75] although the relations advanced between actual sensitizing power and constitution must be regarded as provisional. The term carbocyanines has been assigned by these authors[76] to the important group (of which Pinacyanol = Sensitol Red is the chief) of dyes produced by the condensation of two molecules of quinaldine alkiodide with one of formaldehyde in presence of alkalies. W. H. Mills and F. M. Hammer[77] assign to pinacyanol the constitution



This is derived from its mode of formation, its content of two nitrogen atoms but only one acid equivalent, its molecular weight, and products of oxidation. The 3-carbon linkage :CH.CH:CH is the feature distinguishing carbocyanines from isocyanines. E. O. Adams and H. L. Haller[78] have described a series of dyes, termed kryptocyanines, obtained from lepidine alkyliodides, formaldehyde, and alkali; absorption maximum near 700μμ, sensitizing at 740μμ. A general article on the cyanine dyes is due to O. Fischer and Z. Scheibe[79] while A. and L. Lumière and H. Barbier[80] have described a new series of sensitizing cyanine dyes. Pantochrome from the condensation of dimethylamino-quinaldine with dimethylaminobenzaldehyde showed a nearly uniform action up to 700—, with a slight minimum in the blue-green. Pinaflavol, a new sensitizer for green, is described by E. Konig[81] and J. M. Eder[82] as superior to pinaoverdol.

The effects of isomerism and substitution in the isocyanines, on absorption and sensitizing, are dealt with by F. M. Hammer.[83] The reviewer, from a comparison of his own former work with later experience, cannot regard the values of sensitizing powers given as definitive, since so much depends on purification and methods of sensitizing. On the latter, the article by F. M. Walters and R. Davis[84] and the development of so-called "hypersensitizing" by the use of ammonia, alcohol, and water[85] may be studied. A recent paper by Mills[86] describes a new cyanine type of the benzothiazole series, resembling isocyanines in having a :CH linkage; also analogs of the carbocyanines.

REFERENCES

1—S. E. Sheppard, "Gelatin in the Photographic Process," *J. Ind. Eng. Chem.*, not yet published.

2—Annual Report of the Society of Chemical Industry on Progress of Applied Chemistry, **37** (1918), 465.

3—*J. Ind. Eng. Chem.*, **14** (1922), 130.

4—*J. Chem. Soc.*, **105** (1914), 113.

5—*J. Am. Chem. Soc.*, **38** (1916), 1982.

6—*J. Gen. Physiol.*, **1919** to present date. See also work of Wo. Pauli (*Kolloid chemie d. Eiweiss-korper*, 1st part, **1920**, Steinkopff).

7—"Gelatin in the Photographic Process," *Loc. cit.*

8—*J. Ind. Eng. Chem.*, **14** (1922), 32. *J. Am. Chem. Soc.*, **44** (1922), 1343; *Ibid.*, **44** (1922), 1313.

9—*J. Am. Chem. Soc.*, **41** (1919), 146.

10—Davis and Oakes, *Ibid.*, **44** (1922), 464.

11—S. E. Sheppard and S. S. Sweet, *J. Ind. Eng. Chem.*, **12** (1920), 1007; **13** (1921), 423.

12—*J. Am. Chem. Soc.*, **44** (1922), 373.

13—Brit. Patent 166,063.

14—Brit. Patent 162,266; also Fr. Patents 514,089–92 and 419,863.

15—A. P. H. Trivelli and S. E. Sheppard, "The Silver Bromide Grain of Photographic Emulsions," No. 1 (Monographs on the Theory of Photography, Research Laboratory of the Eastman Kodak Company), **1921.**

16—R. B. Wilsey, *Phil. Mag.*, **42** (1921), 262.

17—*Loc. cit.*, p. 73.

18—*Z. wiss. Phot.*, **18** (1921), 105.

19—*Phot. J.*, **61** (1921), 12.

20—*Ibid.*, **62** (1922), 88.

21—*Brit. J. Phot.*, **1920**, 19.

22—*Phot. J.*, **59** (1919), 260.

23—*Ibid.*, **61** (1921), 333.

24—*Z. wiss. Phot.*, **17** (1920), 36; *Phot. J.*, **61** (1921), 325.

25—*J. Phys. Chem.*, **25** (1921), 81, 561.

26—In press.
27—F. E. Ross, *Astrophys. J.*, **52** (1920), 96.
28—Paper read before American Association Advancement Science, (Toronto), **1921**; *Phil. Mag.*, **44** (1922), 257.
29—*Phil. Mag.*, **44** (1922), 252.
30—"Kolloidchemie u. Photographie," 2nd ed., Dresden, Steinkopff, **1921.**
31—*J. Soc. Chem. Ind.*, **39** (1920), 156T.
32—Luppo-Cramer, *Phot. Korr.*, **57** (1920), 259, 285; S. E. Sheppard, *Brit. J. Phot.*, **68** (1921), 4.
33—Trivelli and Sheppard, *Loc. cit.* Also F. Weigert's valuable work, *Z. physik. Chem.*, **101** (1921), 499.
34—*Phot. J.*, **62** (1922), 186.
35—*J. Franklin Inst.*, **1917**, 705.
36—*J. Soc. Chem. Ind.*, **39** (1920), 2R.
37—Ger. Patents 327,111 and 328,617; O. Mente, *Focus*, **1920**, 168.
38—Lüppo-Cramer, *Phot. Korr.*, **57** (1920), 270.
39—*Chim. et industrie*, **3** (1920), 28.
40—*Rev. franc. Phot.*, **1921**, 237.
41—G. Desalme, *Bull. soc. franc. phot.*, **1910**, 183; Abribat, *Rev. franc. Phot.*, **1921**, Suppl., 50.
42—*Phot. Korr.*, **56** (1919), 387.
43—*Phot. J.*, **60** (1920), 280. A more complete account is to appear as Monograph No. 3 from the Research Laboratory of the Eastman Kodak Company.
44—*Phot. J.*, **60** (1920), 12.
45—*Kolloid. Z.*, **1922**, 114; *Die Photog.*, **1922**, 29; W. Ermen, *Brit. J. Phot.*, **1921**, 445.
46—*Kolloid. Z.*, **1920**, 249; **1921**, 29, 145; also *Phot. Ind.*, **1921**, 550, 716, and *Ibid.*, **1922**, 117.
47—U. S. Patent 1,318,631.
48—U. S. Patent 1,322,580.
49—*Trans. Am. Electrochem. Soc.*, **1921**, 319.
50—*Phot. Ind.*, **1920**, 505, 664.
51—*Ibid.*, **1921**, 378.
52—B. V. Storr, *Phot. J.*, **1921**, 126, and R. Crowther, *Brit. J. Phot.*, **1921**, 3.
53—*Phot. Ind.*, **1921**, 259, 312.
54—*Ibid.*, **1921**, 71.
55—F. A. Elliott, U. S. Patent 1,411,687.
56—A. P. Agnew, *Phot. J.*, **1920**, 121.
57—*Studio Light*, November **1920**; *Courrier du Kodak*, **1921**, 4; *Phot. Chronik*, **1920**, 66, 104.
58—*Koll. Z.*, **1921**, 175.
59—*Phot. Korr.*, **1921**, 282.
60—*Brit. J. Phot.*, **1921**, 6.
61—*Ibid.*, **1920**, 124.
62—*Phot. J.*, **1921**, 450.
63—*J. Chem. Soc.*, **119** (1920), 2048; *Phot. J.*, **1922**, 89.
64—*Helvetica Chim. Acta*, **1919**, 704.
65—*Phot. Korr.*, **1919**, 140.
66—*Phot. J.*, **1920**, 119; Brit. Patent 58,021; Fr. Patent 518,229.
67—*Brit. J. Phot.*, **1921**, 658; Ger. Patent, 337,173.
68—*Phot. Ind.*, **1921**, 439.
69—*Ber.*, **54** (1921), 2111.
70—U. S. Patent 1,331,092.
71—*Brit. J. Phot.*, **1920**, Col. Suppl., 24, 43.
72—Ger. Patent 319,459.
73—Brit. Patent, 147,005, and addition 147,103; *Brit. J. Phot.*, **1921**, Suppl., 23.
74—U. S. Patent 1,389,742.
75—*Phot. J.*, **1920**, 183.
76—*Ibid.*, **1920**, 253.
77—*J. Chem. Soc.*, **117** (1920), 1550.
78—*J. Am. Chem. Soc.*, **42** (1920), 2661; also U. S. Patents 1,374,871–2.
79—*J. prakt. Chem.*, **100** (1919), 86.
80—*Bull. soc. franc. phot.*, **1920**, 182, also Fr. Patents 508,091–2.
81—*Brit. J. Phot.*, **1921**, Col. Suppl., 29.
82—*Phot. Korr.*, **1921**, 29.
83—*Phot. J.*, **1922**, 8.
84—"Methods of Sensitizing by Bathing," *Bur. Standards, Sci. Paper* **422** (1921), 353.
85—S. M. Burka, *J. Frank. Inst.*, **1920**, 24.
86—*J. Chem. Soc.*, **121** (1922), 415.

A course in chemistry is now required in all the schools of the Pennsylvania State College. In the Schools of Agriculture, Engineering, Mines, Natural Science, and Home Economics, various specialized courses are given, while in the School of Liberal Arts only a course in general chemistry is required, though others may be elected. In order that all departments and schools of the college may be expanded in preparation for the development of the institution into the Pennsylvania State University, a campaign for $2,000,000 is now being carried on.

Glass Technology

By George W. Morey

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George W. Morey

THE WAR period preceding that under review was marked by extraordinary activities in the field of glass technology, and it is to be expected that the period of business depression through which we have been passing should show a diminution in activity. While such a diminution has taken place and while no such developments as that of pyrex glass or the remarkable upbuilding of the optical glass industry during the war are to be chronicled, still the development of the industry has been steady and the technologic advances important.

In the line of fundamental research probably the most outstanding contribution has been the comprehensive paper by Adams and Williamson on the annealing of glass, for which the authors were awarded the Longstreth Medal by the Franklin Institute of Philadelphia. Glass annealing is an ever-present problem in all branches of the industry, the solution of which has been in the past groped for in the dark. It had not been realized that "slow cooling" was not sufficient to ensure good annealing; to be sure, slow cooling is essential at a certain stage in the process, but most commercial installations succeed in cooling ware too rapidly in its critical stage, and draw out the cooling to unnecessary lengths when the necessity for control has passed. Adams and Williamson have given a striking illustration of the possibilities in carefully controlled annealing. As is well known, optical glass must satisfy particularly rigid specifications in the matter of strain, and the type of glass known as borosilicate crown is particularly difficult to anneal. Yet by precise furnace control, guided by the very definite rules which they have given, they were able to anneal a slab of borosilicate crown 2 cm. (0.8 in.) thick in 4 hrs. and 50 min. from the time the cold glass was placed in the cold furnace. Annealing problems as difficult as this are not common in practice; yet it is not unusual for days to be given to poorly anneal the more tractable plate glass of the same thickness. By the application of scientific methods superior annealing could be obtained in less time, thereby releasing equipment, increasing production, and decreasing cost. Adams and Williamson's paper is noteworthy in that it not only discusses the annealing of glass from the scientific viewpoint, but also gives explicit detailed instructions for the annealing of various types of glass in various thicknesses. A noteworthy instance of the successful application of these results is the 40-in. reflector disk manufactured in this country during the past year, an achievement described in the June issue of THIS JOURNAL.

The relation of the physical properties of glass to chemical constitution is of fundamental importance in glass technology, and several investigators have been active in this field. In this country the activity is chiefly shown in the number of composition patents that have been issued, including patents on a glass which, while opaque to visible radiation, transmits the infra-red, and also on a glass which, while opaque to the visible, transmits the ultraviolet. An industrial development of technical importance, especially in the application of automatic machines, is the conversion of the electric light bulb from a lead glass to a lime-magnesia glass which can be melted successfully in tanks. Attention should also be called to the work of Peddle, published in the *Journal of the Society of Glass Technology*, which is the most complete and extensive study of the relation between chemical composition and physical properties that has yet appeared. The work to date includes the soda-potash-lime, the soda-potash-lead, and the soda-potash-barium glasses. The physical properties determined are primarily those of interest to the optical glass manufacturer: refractive index, dispersion, comparative "fusibility," and resistance to weathering and to the action of reagents, these latter properties being of importance in all branches of the industry. The important factor of viscosity has not been determined in these extensive experiments, but that is a problem in itself, a problem the study of which is still awaiting the development of a satisfactory technic. Attention is being given this problem, however, both by the manufacturers themselves and by such institutions as the Department of Ceramics of the University of Illinois and the Bureau of Standards, and it is to be hoped that we will soon have not only methods but also data at our disposal. Much additional work is necessary in order to satisfactorily correlate physical properties with chemical constitution, and the subject appears the more difficult as, with the more accurate determination of physical properties, the futility of attempting to represent any property of a glass on a purely colligative basis becomes apparent.

Purely technical developments have followed the lines laid out in previous years. Unfortunately, there is still litigation over some of the important new processes, but final decision has been reached in the "cold bait" patents, of importance in several branches of the glass industry. A development of prime importance, which has been foreshadowed by years of experiment on the part of many firms, is the commercial success of the sheet glass drawing process, which has reached such a stage that 84-in. sheets can now be drawn, and two drawing machines operated from one tank. A striking development has been the rapid extension in the field of application of glass feeders, and the development of several new types, though the Hartford-Fairmount machine still appears to be in the lead. A 15-arm machine of the Owens type for bottle work has been developed. The field of application of automatic machinery has been further extended to bulbs, the manufacture of the latter by machine being now on a commercial basis. The semi-automatic machine has been successfully applied to tumblers and thermos-bottle liners. It appears probable that the next few years will see a still more widespread application of glass feeders and automatic machines, with resulting transformation of the glass industry "from a small scale, many unit skilled craftsman's constant personal triumph over miserably poor and inefficient equipment into an engineering enterprise of first magnitude."[1]

This review has so far confined itself to technical progress, but progress has been made along another line which may in the last analysis prove of more value to the industry as a whole than the more purely material achievements. During the period since the war, there has been developing a spirit of recognition not only of the value of scientific research and control, but also of the value of coöperation and an *esprit de corps*, which bids fair to sweep away the mists of trade secrecy that have in the past oppressed the glass industry. Two new trade journals have appeared, *Glass Industry* and *The Glass Container*. The latter of these is the organ of the Glass Containers Association of America, itself an example of the new spirit in the glass industry. This association is not only supporting a journal, but has taken an active part, with the coöperation of the Bureau of Standards, in the standardization of glass containers, and in encouraging and supporting research. The phenomenal growth of the Glass Section of the American Ceramic Society, the only common meeting ground of glass chemists and technologists in this country, also shows that the men in the glass industry are awakening to a realization that the path to progress is one of respect and coöperation, not one of secrecy and distrust.

Buy Chemicals in Metric Units

FROM time to time the SOCIETY has gone on record as favoring the general use of the metric system. Our committee has accomplished a great deal in having fine chemicals ordered and supplied in metric units, and it is a pleasure now to call attention to the list of dealers prepared to supply standard metric packages.

The Committee on Guaranteed Reagents and Standard Apparatus has recommended that chemicals be handled in multiples of 500 g. Its reports may be found in THIS JOURNAL, **12** (1920), 1206, and **13** (1921), 473. It will be possible to obtain expensive chemicals in smaller packages of 100 g., or even of 25, 5, and 1 g. It is hoped, however, to avoid using the 250- and 50-g. packages. Pure acids and ammonia are being packed in the customary bottles in the following quantities: NH_4OH, 2 kg.; HCl, 2.5 kg.; HNO_3, 3 kg.; and H_2SO_4, 4 kg. When possible they should be ordered by the case (10 bottles).

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C. E. Ising Corp., Flushing, N Y.
Chemical Company of America, New York, N. Y.
Denver Fire Clay Co., Denver, Colo.
Dow Chemical Co., Midland, Mich.
Eastman Kodak Co., Rochester, N. Y.
Eimer & Amend, New York, N. Y.
E. H. Sargent & Co., Chicago, Ill
Emil Greiner Co., New York, N. Y.
Edward P. Dolbey & Co., Philadelphia, Pa.
General Chemical Co. (Baker & Adamson Dept.), Easton, Pa.
Herrick & Voigt, New York, N. Y.
Howe & French, Boston, Mass.
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Palo Co., New York, N. Y.
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Pyrolectric Instrument Co, Trenton, N. J.
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[1] [illegible] and [illegible], *J. Soc. Glass Tech.*, 5 (1921), 152.

Review of Analytical Work Applicable to Leather and Tanning, 1920-1921[1]

By F. P. Veitch and R. W. Frey

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PROBABLY few, if any, of our important industries offer to chemists as fertile a field for research and scientific work as does that of tanning. Certainly in no other industry is so little known of the composition of the principal raw materials and of the mechanism and control of the fundamental processes. In the past few years, however, there has been an increasing interest and activity in leather and tanning chemistry which is indeed gratifying, and it is hoped this will continue until the art of tanning has been put on a sound scientific basis.

Many problems of analytical nature are still unsolved and probably will remain so until there is a better knowledge of the fundamentals involved. Progress in this branch, however, can certainly be claimed, as will be readily realized from the following review of work done in the short space of two years.

R. W. Frey

Tannin Analysis

In this country the work of Wilson and Kern on the hide powder method of tannin analysis has redirected attention to fully recognized sources of error in this method and has also revived considerable interest in the subject by the rather startling results obtained. In their first paper[1,*] they describe a method which consists essentially of shaking the tannin solution with purified hide powder until all tannin, as determined by the gelatin-salt test, has been removed from solution. The tanned hide powder is then washed free from soluble matter, dried, and analyzed for tannin as in the regular procedure for vegetable tanned leathers, and from this figure the percentage of tannin in the original material is calculated. Figures from comparative analyses of 8 common tanning materials by this new method and by the official hide powder method of the American Leather Chemists Association are from 43 per cent to 220 per cent higher for tannin by the latter method, due chiefly to the removal by this method of nontannins, such as gallic acid, pyrocatechol, and so on, which do not make leather and are readily washed out. The presentation of Wilson and Kern's paper brought forth considerable discussion[2] in opposition to it and also quite a controversy between the authors and Schultz and Blackadder.

The two last-named authors[3] in a detailed study of the new method take exception to several assumptions involved in it and give data to indicate that two are in error: namely, "that there is a definite chemical compound formed between the tannin in the tannin solution and the collagen in the hide powder during a 6-hr. shaking, which chemical compound is stable with regard to water and also insoluble in water;" and "that one definite chemical compound is formed throughout the whole of the hide powder used in the analysis." They show particularly that from the washings of the tanned hide powder a certain amount of tannin can be recovered as determined by the new method and that the tanned hide powder is very heterogeneous physically, being made up roughly of a distinctly fibrous portion and a relatively fine powdery portion. The last is more heavily tanned than are the coarser particles and being so very fine is apt to be lost during washing. The loss of this relatively tannin-rich powder leaves the residue proportionally poorer in tannin and causes a loss of tannin as determined by the new method.

In further defense of their new method Wilson and Kern[4] give data to show that tannin once combined with hide cannot be washed out by any amount of washing that would be practical, and that concentration of the nontannins and washings from the tanned hide powder converted certain nontannins into substances capable of tanning.

In continuation of the controversy Schultz[5] presented a very elaborate study showing that the detannized solution and washings according to Wilson and Kern's method contain materials which, without concentration, will combine with hide powder and be resistant to washing. An experiment is also described which indicates that concentration does not bring about a chemical change with conversion of nontannins into tanning materials, and according to Schultz such phenomena are probably explained by the dispersed state of the tannin under various conditions. Results from a rather extensive series of experiments, involving a strict comparison of the basic principles of the official hide-powder method and of the new one, show that the effects of the three factors influencing the absorption of tannin by hide powder, namely, the amount of hide powder, concentration of tannin, and volume of solution, are as pronounced after washing the tanned hide powder as they are without washing. Schultz concludes that the Wilson and Kern method of tannin analysis is based on a series of false assumptions and gives neither the true value of tanning materials nor the true tannin content.

Since considerable objection was raised to the Wilson and Kern method on the ground that it was too cumbersome and time-consuming, these two authors presented a modification[6] which greatly simplified their procedure and also removed several possible sources of manipulative errors which previously had been pointed out. Comparative analysis, by the original and revised procedures, however, of 6 typical extracts gives practically identical results Replying to the work of Schultz, Wilson and Kern[7] refute many of his objections and particularly show that the new method will give the same tannin figure for varying quantities of hide powder. Answering this paper Schultz[8] gives further argument against the work of Wilson and Kern and in support of his findings.

Baldracco and Camilla[9] have proposed a modification of the official method of tannin analysis of the Society of Leather

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[*] Numbers in the text refer to Bibliography at end of paper.

Trades' Chemists using a prepared, lightly chromed hide powder. It is contended that the usual washing of hide powder removes acid which is necessary for complete combination of the tannin and hide powder, and that ready chromed hide powder as prepared by them[10] always contains sufficient acid for complete detannizing and is much more convenient to use. Schell[11] in criticism of the work of Baldracco and Camilla states that their tannin figure includes more nontannin than in the case of the official method and that their method is not as exact nor is the hide powder they propose as well defined as the official one. Lauffmann[12] claims that the reagents used by Baldracco and Camilla are not suitable as they give similar reactions for tannins, and also that proof has still to be produced that hide powder with the filter method absorbs materials which should really be estimated as nontannins. In reply Baldracco and Camilla[13] point to their previous work showing that tanning by the filter method is too high as some nontannins are absorbed, while by the official shake method of the International Association of Leather Trades' Chemists the tannic acid is not all removed from certain extracts.

Moeller[14,15] has done considerable work on the error in nontannin determinations due to the presence of hydrolyzed hide substance. Determination of the dissolved hide substance in the nontannin residues from about 50 tanning materials showed that it usually amounted to several per cent of the nontannin residue. Parker and Terrell[16] in some notes on the filtration of tanning solutions show the superiority of the filter candle to filter paper, as the latter continues to absorb soluble matter even after considerable quantity of solution has passed through. Thompson, Seshachalam, and Hassan[17] have shown that in tannin analysis the time of filtration, color, tannin content, insolubles and so on are all liable to considerable variation with different degrees of acidity. Sollmann[18] in studies on the precipitation of proteins by tannin has determined that in concentration (0.1 to 0.5 per cent) necessary to produce astringent action, precipitation is greatest at a pH of 2 to 5. There is no precipitation when the alkalinity is pH 8 to 8.3.

Frey and Clarke[19] have proposed a practical simplification and shortening of the washing of chromed hide powder for tannin analysis and give data to show that results are in agreement with those from official practice. The report of the British tannin analysis committee[20] shows that in washing the chromed hide powder only distilled water should be used. Baldracco and Camilla[1c] have described the preparation of a ready chromed hide powder.

LEATHER ANALYSIS

VEGETABLE TANNED LEATHERS—A committee of the American Leather Chemists' Association under the chairmanship of Small[21] has gone very thoroughly into the subject of the sampling of leather and its preparation for analysis. This excellent report gives complete analysis of the leather from all parts of hides and sides of various tannages, thus emphasizing the variations in composition and showing what sections to combine for the most representative sample. From these data a chart has been prepared showing the locations for sampling of all commercial trims. A French committee on leather analysis, with Chambard[22] as chairman, has also done some work which shows a large zone between the shoulder and butt of nearly constant composition and recommends sampling [illegible]

Veitch and Jarrell[23] in a detailed study of the determination of moisture in leather show particularly the influence of atmospheric humidity. With ungreased leathers a difference of 35 per cent relative humidity gives on the average a difference of 0.5 per cent in drying losses. It is also shown that repeated drying of leather at constant humidity gives a progressive loss in weight; that the electric oven at 100° C. gives results slightly higher than the combined evaporator and drier; and that the vacuum oven at 70° C. gives results lower than the drier or electric oven at 100° C., but at 97° to 98° C. gives higher results.

The determination of hide substance in leather has been studied by several workers. Chambard[24] considers incomplete oxidation and too small a charge of leather as the most likely sources of error. He obtains good results with a modification of the Kjeldahl method as for silk analysis using a relatively large sample (2.8 g.) of leather and digesting with sulfuric acid, potassium bisulfite, and anhydrous copper sulfate. F. G. A. Enna[25] proposes a rapid method using a drop of mercury which is afterwards precipitated out. Cochrane,[26] from work on feeds and feces, shows that the addition of permanganate does not cause a loss of nitrogen and that using the same method without the addition of permanganate results are less concordant and uniformly lower. Kahn[27] considers as important sources of error in the Kjeldahl method the following: lack of uniformity of the powdered leather; insufficient decomposition; the possibility of alkali, acid or particles of zinc being carried over in the distillation; and of some ammonia escaping with the air bubbles. Parker and Terrell[28] have investigated the use of perchloric acid in Kjeldahl digestions of leather and have found that it gives satisfactory results and considerably shortens the time of digestion.

Active work both here and abroad has been continued on the much-mooted question of a suitable solvent for the extraction of oils and greases from leather. Two English committees[29] have compared numerous solvents from which they conclude that either chloroform or benzene should be officially adopted with preference for the latter if the color of the extract is of importance. Veitch and Clarke[30] have summarized previous work on the subject and give data on the extraction, particularly of soaps, in leather. It is shown that the presence of moisture increases the quantity of soap fats extracted by chloroform and petroleum ether; that the presence of tannic acid increases the solubility of soap fats very greatly, especially in chloroform; that magnesium salts added to leather will lead to the extraction of the soap as a whole if opportunity is given for the formation of magnesium soaps, since these are very soluble in both chloroform and petroleum ether; and that calcium soaps are extracted by chloroform in a colloidal state but are practically insoluble in petroleum ether.

A committee report of the American Leather Chemists' Association by Terrassee and Anthes[31] on water-solubles in leather gives the results of a study of the official method from which it is concluded that the sample should be finely ground and freed from grease and that the extraction should be carried out in a specified apparatus on 30 g. of leather at 50° C. Two liters of extract should be collected in three hrs. without any previous period of soaking. A later committee under the chairmanship of Wilson[32] undertook to study primarily the influence of temperature and whether or not a definite end-point could be reached in the water extraction of leather. The committee results showed very little agreement on these two points. Apropos of the subject, Veitch and Frey[33] have published some notes showing that there is no absolute end-point even for a 148-hr. extraction but that the extraction appears to settle down to a practically constant value.

A subject for considerable work has been the determination of glucose in leather. Rogers[34] as chairman of an American Leather Chemists' Association committee made quite an elaborate report showing that five drops of toluene per liter will preserve leather extracts for at least three days without loss of sugar; that when sodium carbonate is used for neutralization after hydrolysis in the presence of Epsom salts high results are obtained because of the precipitation of magnesium; that caustic soda if used in excess will precipitate the magnesium; that there does not appear to be any advantage in using stronger solutions for analysis; and finally, a point of considerable importance, that low results when using sodium hydroxide for neutralization are possibly not due to any action of the sodium hydroxide on the dextrose but to sodium plumbite which has a reducing action on the sugar. Continuing his committee work, Rogers[35] sought the best reagent for complete removal of lead and as a result recommended that a strong solution of disodium acid phosphate be made the object of further study. To shorten the time for sugar determination van der Hoeven[36] has proposed a volumetric procedure which is a modification of Schoorl's method. Quisumbing and Thomas[37] have made a very thorough, careful study of conditions affecting the determination of reducing sugars and have proposed a procedure which eliminates most sources of error.

In the determination of magnesium in leather Frey[38] has shown that Epsom salts determined from the ash of the leather ranges from 0.05 per cent to 0.25 per cent higher than when determined from the water extract and also that Epsom salts either alone or in solution in the water extract loses practically 40 per cent of its weight upon 16 hrs.' drying in the evaporator and dryer. The work of an American Leather Chemists Association committee with Frey[39] as chairman has shown that the volumetric procedure for magnesium as outlined by Handy gives results in agreement with those by the gravimetric method.

For the determination of sulfuric acid in leather Thomas[40] has proposed quite a departure from the usual suggestions. The principle of his method is based on the displacement of the sulfuric acid by ions of a higher valence and is effected by digestion of the leather with potassium dihydrogen phosphate solution. A modification of this same method is also given by Thomas and Frieden[41] for the determination of hydrochloric acid and neutral chlorides in leather.

MINERAL TANNED LEATHERS—Hou[42] in some experiments on the volumetric determination of chromium in leather by the sodium peroxide fusion method has emphasized the need of taking the fusion solution down to a small volume to insure decomposition of all peroxide and also of controlling the acidity of the solution for titration. An English committee, of which Innes[43] was chairman, has reported on methods which they have so far found best for the analysis of chrome leather. Brgeniner[44] has made a detailed study of the methods and factors influencing the determination of chromium.

Grasser,[45] one of the pioneer workers in iron tanning, has published a quite complete article on the subject and given methods for control analysis.

VEGETABLE TAN LIQUORS—Claflin[46] has proposed a very practical method for determining the plumping power of tanning solutions, which consists essentially of measuring the volume of solution absorbed by hide powder under properly controlled conditions. The simplicity of his method, together with the practical value of results by it, has proved very attractive. Working along the same line McLaughlin and Porter,[47] using pieces of limed and hydrated steer hide instead of hide powder, have made a study of the swelling of white hide in tan liquors, dealing particularly with the usual organic acids and calcium acetate and lactate. Their results emphasize the significance of direct results obtained in this manner. Atkin and Thompson[48] have published a very informing paper on the determination and control of the acidity of tan liquors by a colorimetric method using indicators.

Blackadder,[49] in a report on the color measurement in tanning solutions, describes some experiments with a tint photometer, from which he is inclined to conclude that any use of blue in a combination of color to match a tanning solution is unnecessary and may lead to error; and that while an apparatus based on matching a built-up color standard against an unknown color will not prove satisfactory, a machine based on spectrum analysis ought to be capable of adaptation. Wilson and Kern[50] have shown an interesting relation between the hydrogen-ion concentration of a tan liquor and its color value. Tan liquors change in color with change in pH value over a range from 3 to 12 and this change in color is completely reversible if the liquors are not long exposed to air. Liquors exposed to air continue to darken, with accompanying rise in the pH value, but this change is not reversed by lowering the pH value. Exposed to air at pH values of about 9, liquors give bulky precipitates when their pH values are brought to 3.

CHROME LIQUORS

The analysis of chrome liquors has apparently been a subject of considerable interest. Thomas and Foster[51] have described a conductance-barium hydroxide titration method for chrome liquors which "is to be preferred to the American Leather Chemists Association titration method not only on account of theoretically truer results but also convenience." Adsorbed chromic sulfate in the precipitated hydrous chromic oxide is the chief cause of low results by the American Leather Chemists Association titration method. Dhavale and Das,[52] from detailed experiments incidental to an investigation of the effect of neutral salts on the basicity of chrome liquors, have shown that the addition of sodium chloride causes a marked increase in the acidity of chrome liquors as found by the Procter and McCandlish method and also that the values obtained by this method are influenced by the temperature of titration and speed of adding the alkali but not by the dilution of the liquor under titration. Thomas and Foster[53] also deal with the effect of salt on the titration of chrome liquors and give some data which indicate that the alkalimetric titration method for acidity of chrome liquors could be made to yield more correct results by the addition of about 50 g. of sodium chloride before titrating. Burton and Hey,[54] in the course of investigations on chrome tanning, have pointed out the influence of carbon dioxide, sulfur dioxide, and volatile acids on the American Leather Chemists Association method of titrating acidity of chrome liquors, showing that it is inadequate since it fails to take these into account, and they have recommended that the titration be made by adding the caustic soda to the diluted liquor in the cold and by continuing the addition of alkali during the period of heating up to the boiling point. Pickering[55] has pointed out several precautions to be taken in determining basicity figures for chrome liquors, describing also a means of illumination for a clear end-point in titrating. Schorlemmer[56] and Grasser[57] have both discussed and suggested systems for expressing the basicity of chrome liquors. Thomas and Kelly[58] have proposed a rapid estimation of chromium in chrome liquors by means of the immersion refractometer.

LIME AND LIME LIQUORS—English committees on lime-yard control under Burton,[59] Atkin and Palmer,[60] Pickles,[61] and Atkin and Atkin[62] have been very active in reviewing, criticizing, and proposing methods best suited for lime liquor analysis. F. G. A. Enna[63] has described a method for determining the available sulfide in a lime liquor based on the fact that a quantitative separation of hydrogen sulfide from its alkaline salts is effected by carbonic acid, while thiosulfates and amino acids are unaffected. Singer[64] has made a comparative study of various methods for analysis of lime liquors.

Grasser[65] has pointed out the advantages of determining lime in unhaired skins from solution by wet oxidation rather than from solution of the ash. Veitch and Jarrell[66] have reviewed the various methods for determining available calcium oxide in lime and after considerable study have proposed and outlined in detail modifications of the tannery method and Scaife method so as to insure accurate and concordant results.

IDENTIFICATION OF TANNING MATERIALS

Grasser[67] has published some very interesting observations on the behavior of various tanning materials during electrodialysis which may be developed for the identification of tannins. Lauffmann[68] has discussed in detail the tests for the identification and examination of tanning materials and extracts. Lauffmann[69] has also described a modification of the indophenol reaction so that it can be used for identification of that class of synthetic tannins formed by the condensation of formaldehyde with the sulfonic acids of phenol, cresol, naphthalene or anthracene.

De Hesselle[70] has published a modification of Appelius and Schmidt's cinchonine test for sulfite-cellulose. With this test certain synthetic tannins react partially like vegetable tannins; others like sulfite-cellulose; and some do not give the reaction at all. Hough[71] has described a method for determining bisulfites in extracts.

For differentiation between old fustic and quercitron extracts Justin-Mueller[72] has found that the ether extracts upon solution in sulfuric acid and dilution with water remain bright orange-yellow for old fustic but are decolorized for quercitron. Atkin and Marriott[73] have shown that the application of polarized light in the microscopical analysis of sumac gives more definite and quicker results than does the ordinary microscopical procedure. Groll[74] has published considerable data on gambier and its adulteration, and Jablonski and Einbeck[75] have done likewise for quebracho, emphasizing particularly the value of a fluorescein reaction for its detection. Mimosa extract, however, gives a similar reaction.

SULFONATED OILS

A committee of the American Leather Chemists Association, with Schultz[76] as chairman, has made quite a study of the determination of combined SO_3, total fatty matter and neutral fat in sulfonated oils. Hart[77] has published a method and formula for the determination of inorganic impurities in sulfated oils, which formula he improved in a later paper.[78] Bunicke[79] has also offered an improvement of the Hart method. Pickering[80] has done considerable work on methods for the commercial examination of sulfonated oils. Kern[81] has proposed the determination of sulfate in sulfonated oils by means of a solution of monosodium phosphate which will give a practically complete separation of oil from solution with sulfonated oil without the addition of a solvent and will extract all of the free and none of the combined sulfate.

MISCELLANEOUS

Thomas[82] has described some experiments on estimating the tryptic activity of bating materials, using two methods developed from the work of Sherman and Neun. Matos[83] has discussed the testing of dyes in the leather industry. Welwart[84] has given a method for determining ammonia in oil and fat preparations. Hoffman[85] has proposed a means of detecting and separating lactic acid as a complex sodium ferric lactate. Froboese[86] has dealt in considerable detail with the examination of leather substitutes. Bogue[87] has published a very comprehensive article on glues and gelatins, giving a most complete and excellent bibliography on the subject.

BIBLIOGRAPHY

1—Wilson and Kern, *J. Ind. Eng. Chem.*, **12** (1920), 465; *J. Am. Leather Chem. Assoc.*, **15** (1920), 295.

2—Discussion, *J. Am. Leather Chem. Assoc.*, **15** (1920), 451.

3—Schultz and Blackadder, *Ibid.*, **15** (1920), 654.

4—Wilson and Kern, *J. Ind. Eng. Chem.*, **12** (1920), 1149; *J. Am. Leather Chem. Assoc.*, **16** (1921), 75.

5—Schultz, *J. Am. Leather Chem. Assoc.*, **16** (1921), 349.

6—Wilson and Kern, *J. Ind. Eng. Chem.*, **13** (1921), 772; *J. Am. Leather Chem. Assoc.*, **16** (1921), 622.

7—Wilson and Kern, *J. Am. Leather Chem. Assoc.*, **16** (1921), 631.

8—Schultz, *Ibid.*, **16** (1921), 637.

9—Baldracco and Camilla, *Cuir*, **9** (1920), 257; *J. Soc. Leather Trades' Chem.*, **4** (1920), 101.

10—Baldracco and Camilla, *Cuir*, **9** (1920), 152; *J. Soc. Leather Trades' Chem.*, **4** (1920), 88.

11—Schell, *Cuir*, **9** (1920), 327.

12—Lauffmann, *Ledertech. Rundschau*, **12** (1920), 95.

13—Baldracco and Camilla, *Collegium*, **611** (1921), 125.

14—Moeller, *Ibid.*, **603**, 307; **604**, 374.

15—Moeller, *Z. Leder u. Gerb. Chem.*, **1** (1921), 28.

16—Parker and Terrell, *J. Soc. Leather Trades' Chem.*, **5** (1921), 112.

17—Thompson, Seshachalam and Hassan, *Ibid.*, **5** (1921), 389.

18—Sollmann, *J. Pharmacol.*, **16** (1920), 49.

19—Frey and Clarke, *J. Am. Leather Chem. Assoc.*, **16** (1921), 477.

20—British Committee, *J. Soc. Leather Trades' Chem.*, **5**(1921), 274.

21—Small, *J. Am. Leather Chem. Assoc.*, **16** (1921), 394.

22—Chambard, *J. Soc. Leather Trades' Chem.*, **5** (1921), 313; *Cuir*, **10** (1921), 418.

23—Veitch and Jarrell, *J. Am. Leather Chem. Assoc.*, **16** (1921), 547.

24—Chambard, *J. Soc. Leather Trades' Chem.*, **4** (1920), 159.

25—Enna, *Collegium*, **601** (1920), 207.

26—Cochrane, *J. Ind. Eng. Chem.*, **12** (1920), 1195.

27—Kahn, *Collegium*, **604** (1920), 367.

28—Parker and Terrell, *J. Soc. Leather Trades' Chem.*, **5** (1921), 380.

29—English Committees, *Ibid.*, **4** (1920), 7, 300.

30—Veitch and Clarke, *J. Am. Leather Chem. Assoc.*, **16** (1921), 458.

31—Terrassee and Anthes, *Ibid.*, **15** (1920), 581.

32—Wilson, *Ibid.*, **16** (1921), 264.

33—Veitch and Frey, *Ibid.*, **16** (1921), 491.

34—Rogers, *Ibid.*, **15** (1920), 411.

35—Rogers, *Ibid.*, **16** (1921), 480.

36—van der Hoeven, *Collegium*, **613** (1921), 220.

37—Quisumbing and Thomas, *J. Am. Chem. Soc.*, **43** (1921), 1503.

38—Frey, *J. Am. Leather Chem. Assoc.*, **15** (1920), 406.

39—Frey, *Ibid.*, **16** (1921), 595.

40—Thomas, *Ibid.*, **15** (1920), 504.

41—Thomas and Frieden, *J. Ind. Eng. Chem.*, **12** (1920), 1186; *J. Am. Leather Chem. Assoc.*, **16** (1921), 2.

42—Hou, *J. Am. Leather Chem. Assoc.*, **15** (1920), 367.

43—Innes, *J. Soc. Leather Trades' Chem.*, **4** (1920), 294.

44—Brgeniner, *Z. anal. Chem.*, **59** (1920), 241; *Ann. chim. anal.*, **2** (1920), 339; *Cuir*, **10** (1921), 15.

45—Grasser, *Collegium*, **600** (1920), 3; *Cuir*, **9** (1920), 472.

46—Claflin, *J. Am. Leather Chem. Assoc.*, **15** (1920), 234.

47—McLaughlin and Porter, *Ibid.*, **15** (1920), 557.

48—Atkin and Thompson, *J. Soc. Leather Trades' Chem.*, **4** (1920), 143.

49—Blackadder, *J. Am. Leather Chem. Assoc.*, **16** (1921), 280.

50—Wilson and Kern, *J. Ind. Eng. Chem.*, **13** (1921), 1025.

51—Thomas and Foster, *J. Am. Leather Chem. Assoc.*, **15** (1920), 510.

52—Dhavale and Das, *J. Soc. Leather Trades' Chem.*, **4** (1920), 225.

53—Thomas and Foster, *J. Am. Leather Chem. Assoc.*, **16** (1921), 61.

54—Burton and Hey, *J. Soc. Leather Trades' Chem.*, **4** (1920), 272.

55—Pickering, *Ibid.*, **5** (1921), 177.

56—Schorlemmer, *Collegium*, **607** (1920), 536.

57—Grasser, *Ibid.*, **615** (1921), 319.

58—Thomas and Kelly, *J. Am. Leather Chem. Assoc.*, **15** (1920), 665.

59—Burton, *J. Soc. Leather Trades' Chem.*, **4** (1920), 32.

60—Atkin and Palmer, *Ibid.*, **4** (1920), 111.

61—Pickles, *Ibid.*, **4** (1920), 231.

62—Atkin and Atkin, *Ibid.*, **4** (1920), 236.

63—Enna, *Ibid.*, **5** (1921), 131.

64—Singer, *Cuir*, **10** (1921), 356.

65—Grasser, *Collegium*, **598** (1920), 80.

66—Veitch and Jarrell, *J. Am. Leather Chem. Assoc.*, **16** (1921), 438.

67—Grasser, *Collegium*, **597** (1920), 17; **598** (1920), 49; **600** (1920), 137; **601** (1920), 200.

68—Lauffmann, *Ledertech. Rundschau*, **13** (1921), 65, 73.

69—Lauffmann, *Collegium*, **600** (1920), 169.

70—De Hessele, *Ibid.*, **618** (1921), 425.

71—Hough, *Cuir*, **9** (1920), 162.

72—Justin-Mueller, *Bull. soc. chim.*, **27** (1920), 844.

73—Atkin and Marriott, *J. Soc. Leather Trades' Chem.*, **5** (1921), 275.

74—Groll, *Ber. Afdeelinghand, Koloniaal Inst.*, No. 3 (1920).

75—Jablonski and Einbeck, *Ledertech. Rundschau*, **13** (1921), 41.
76—Schultz, *J. Am. Leather Chem. Assoc.*, **15** (1920), 283.
77—Hart, *Ibid.*, **15** (1920), 404.
78—Hart, *Ibid.*, **16** (1921), 159.
79—Bunicke, *Ibid.*, **16** (1921), 7.
80—Pickering, *J. Soc. Leather Trades' Chem.*, **39** (1920), 305.
81—Kern, *J. Ind. Eng. Chem.*, **12** (1920), 785.
82—Thomas, *J. Am. Leather Chem. Assoc.*, **15** (1920), 221.
83—Matos, *Ibid.*, **15** (1920), 553.
84—Welwart, *Chem. Ztg.*, **44** (1920), 719.
85—Hoffman, *Ber.*, **53** (1920), 224.
86—Froboese, *Z. Nahr.-Genussm.*, **41** (1921), 113.
87—Bogue, *Chem. Met. Eng.*, **23** (1920), 5, 61, 105, 154, 197.

Vegetable Tanning

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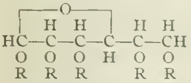
THE NATURE of tannin has been under study by organic chemists for many years, but the outstanding feature of organic chemical investigation was the synthesis of gallotannic acid (the tannin of oak galls) by Emil Fischer in 1918,[1] which rendered all previous work practically obsolete.

The study of the hydrolytic products of purified nutgalls tannin showed that 1 molecule of glucose was combined with a number of molecules of gallic acid, and that gallotannic acid was actually a pentadigalloyl glucose, with the formula



$$\begin{array}{cccccc} \multicolumn{4}{c}{\overbrace{\qquad\qquad\qquad}^{O}} & & \\ & H & H & & H & H \\ HC- & C- & C- & C- & C- & CH \\ O & O & O & H & O & O \\ R & R & R & & R & R \end{array}$$

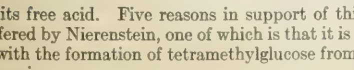
where R = digalloyl radical.

By condensing 5 molecules of tricarbomethoxygalloyl chloride with 1 molecule of glucose in the presence of quinoline (the carbomethoxy groups protecting the hydroxy groups of the gallic acid from the action of phosphorus pentachloride) and the carbomethoxy groups being subsequently removed by cold alkali, pentadigalloyl glucose, similar in properties to gallotannic acid, was obtained.

Fischer also prepared a series of acyl glucoses, many of which have tanning properties. The monacyl glucoses do not precipitate gelatin, but trigalloylglucose shows pronounced tanning properties. Trigalloylglycerol and hexagalloylmannitol precipitate gelatin in aqueous solution.

Fischer prepared penta-*m*-digalloyl-β-glucose, which was proved to be an isomer of Chinese tannin, and in the first paper mentioned he proved that the "glucogallin" isolated by Gilson from Chinese rhubarb is 1-galloyl-β-glucose.

Nierenstein[2] raises a number of objections to Fischer's formula, mainly on the ground that whereas Fischer's pentadigalloylglucose when methylated with diazomethane yields glucose on hydrolysis, methylogallotannin gives under identical conditions tetramethylglucose, showing that in gallotannin 4 hydroxyl groups are not replaced by digalloyl radicals. Nierenstein proposes a modified long chain formula based on the supposition that gallotannin is probably a glucoside of the following polydigalloylleuco-digallic acid anhydride:



$$\begin{array}{l} (OH)_3C_6H_2.CO.[O.C_6H_2(OH)_2.CO]x \\ \quad .O.\underset{\displaystyle O\text{———————————————}}{\underset{|}{C_6H_2}}(OH).CO.O.C_6H_2(OH)_2.CH(OH).O.\underset{\displaystyle CO}{\underset{|}{C_6H_2}}(OH)_2 \end{array}$$

or of its free acid. Five reasons in support of this formula are offered by Nierenstein, one of which is that it is in accordance with the formation of tetramethylglucose from methylogallotannin.

Nierenstein is also studying the constitution of the catechu tannins. He has recently found[3] that Paullinia tannin from *Paullinia cupana* seeds is a crystalline normal glucoside consisting of 1 molecule of dextrose and 2 molecules of gambier-catechin-carboxylic acid, forming a depside.

K. Freudenberg, formerly associated with Fischer, is continuing that great master's work on the tannins. He has shown[4] that Hamameli tannin, which has been isolated in the crystalline condition, yields on hydrolysis with tannase gallic acid and an unidentified aldo-hexose in the proportions required for a digalloylhexose.

Freudenberg's investigations[5] of chebulinic acid, which occurs in myrabolans, showed that it is a crystalline material sparingly soluble in cold water, which cannot be hydrolyzed by tannase, and that it is probably a compound of a digalloylglucose and a new phenolic acid, the latter forming a glucoside with the glucose. He showed[6] chlorogenic acid, the tannoid constituent of coffee, to be a simple depside of caffic and quinic acids. Gambier-catechin has been shown[7] to have an oxydiphenylpropane nucleus, to be related to the flavone dyes and anthocyanidins, thus disproving an older view that it was a derivative of ethyldiphenylmethane.

The tannins of the woods of the Spanish chestnut and native German oak have recently been found by this same chemist[8] to contain quercitrin, glucose, and ellagic acid.

The leaves of *Acer ginnala* yield a crystalline tannin, acertannin, $C_{20}H_{20}O_{13}$, and an amorphous mixture consisting of ellagic acid, quercitrin, an amorphous tannin, mainly galloyl-aceritols with small amounts of a flavonol glucoside, and a substance probably a phlobo-catechol tannin according to Perkin and Uyeda.[9] Acertannin hydrolyzes to 2 molecules of gallic acid and a dextrorotatory sugar, aceritol. Aceritol behaves as a polyhydric alcohol and is probably an anhydrohexitol derived from mannitol or sorbitol.

A new classification of natural tannins, more discriminating than the older pyrogallol-catechol categories, has been proposed by Perkin and Everest:[10]

1—Depsides (old gallotannins).
2—Diphenyl methoid (old ellagitannins).
3—Phlobatannins (old catechol tannins).

Freudenberg[11] has recently offered a classification much more distinctive than the above:

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[1] *Ber.*, **51** (1918), 1760; **52** (1919), 829.

[2] *J. Soc. Chem. Ind.*, **41** (1922), 29T.

[3] *J. Chem. Soc.*, **121** (1922), 23.

[4] *Ber.*, **52** (1919), 177; **53** (1920), 953.

[5] *Ibid.*, **52** (1919), 1238.

[6] *Ibid.*, **53** (1920), 232.

[7] *Ibid.*, **53** (1920), 1416.

[8] *Ibid.*, **54** (1921), 1695; *Naturwissenschaften*, **8** (1920), 905.

[9] *J. Chem. Soc.*, **121** (1922), 66.

[10] "The Natural Organic Coloring Matters," Longmans, Green & Co., New York, **1918**.

[11] "Die Chemie der Natürlichen Gerbstoffe," Julius Springer, Berlin, **1920**.

1—Hydrolyzable tannins in which the benzene nuclei are united to larger complexes through oxygen atoms.

2—Condensed tannins, in which the nuclei are held together through carbon linkages.

Where both kinds of compounds are present in the molecule, *e. g.*, in ellagic acid, the classification is decided according to the genetic connection with other tannins.

Group 1 embraces (*a*) esters of phenolcarboxylic acids with each other or with other oxyacids (depsides), (*b*) esters of phenolcarboxylic acids with polyatomic alcohols and sugars (tannin class), and (*c*) glucosides. The most important criterion for Group 1 is hydrolysis to simple components by enzymes, particularly tannase or emulsin.

Tannins of Group 2 are not decomposed to simple components by enzymes. They are generally, but not always, precipitable by bromine, and when treated with oxidizing agents or strong acids condense to high molecular amorphous tannins or "reds." They are divided into two classes according to whether or not phloroglucin is present. With the exception of some simpler ketones, oxybenzophenones and oxyphenylstyrylketones, the catechines belong to the phloroglucin, class, *e. g.*, the very important quebracho, and probably oak tannin are in this class.

Freudenberg has made valuable use of the enzyme tannase secreted by *Aspergillus niger*. A recent paper by him and Vollbrecht discusses the isolation and determination of the activity of this enzyme.[12] For a complete summary of the present knowledge of the organic chemistry of natural tannins Freudenberg's very valuable book[11] should be consulted.

ELECTROLYSIS OF TANNINS

Extensive studies of the conduct of tannins upon electrolysis have been made by Grasser,[13] but the results are greatly confused due to oxidation, reduction, and decomposition. He found that mangrove and catechin are sodium salts, and that in some instances a separation of two qualitatively different tannins can be effected by electrophoresis.

Wilson,[14] in extension of his application of the Procter-Wilson theory of tanning,[15] discusses the reasons for the different degrees of astringency of tannins, and attributes the great difference of astringency between quebracho and gambier to the differences in the electrical charges of the particles and to the content of non-tans. He found that quebracho became mild in action when gallic acid was added to it, and suggested the mechanism for the fixation of tannins by hide substance.

Thomas and Foster[16] actually measured the electrical charge of eight different vegetable tanning materials by the U-tube electrophoresis method. They found all to be anodic in migration (at their natural reaction, *i. e.*, $-\log C_{H^+} =$ ca. 4.) and that the potential difference of the Helmholtz double layer of astringent quebracho was the highest, namely, −0.028 volt, while that of mildly acting gambier was the lowest, −0.005 volt. This confirms the theory of Wilson that astringency is a function of the electrical charge.

Thomas and Foster also showed that the negative electrical charge of quebracho could be gradually reduced and finally brought to zero by addition of small amounts of hydrochloric acid, while the charge for this tanning material, as well as for four others, was raised by removal of the non-tans by dialysis: as, for example, cube gambier showed a p. d. of −0.005 volt in natural state; after dialysis for 24 hrs. it became −0.024 volt. This shows that the non-tans have a profound effect upon the p. d. of the tannin particles, and partly resolves Wilson's two explanations of astringency to one and the same thing, although it must be noted that the charge is not the sole factor in fixation by pelt, since undoubtedly one mechanism of the non-tans in reducing astringency lies in their high diffusive power and loose fixation in the pelt, thus preventing "case hardening" by the tannins and retarding and evening the fixation of the same.

The significance of H$^+$ ion to the charge of tannin particles was indicated in the paper by Thomas and Foster, and a continuation of the study of this question is in progress. Considerable data on the influence of electrolytes in precipitation of tannins are also given in this paper, throwing light on their colloidal properties.

FIXATION OF TANNINS BY PELT

A study of the time and concentration factors in the fixation of tannins by pelt is being pursued by Thomas and Kelly, a preliminary paper on quebracho and gambier having appeared recently.[17] This paper shows a striking difference between the action of astringent quebracho and mild gambier. The concentration curves for gambier rise regularly and slowly like the well-known "adsorption curve," while those for quebracho rise very steeply to a maximum at 30 to 40 g. total solids per liter of solution and then drop off abruptly. They explain this action of quebracho by the fact that owing to the lack of non-tans in this astringent material the surfaces of the hide substance particles are so heavily tanned that they are rendered impermeable to tannin and hence the interiors are unaffected, thus accounting for the smaller amount of tannin fixed by the hide in the strong solution.

Wilson and Kern[18] have shown that prolonged washing with water neither hydrolyzes vegetable leather nor removes any of the tannin therefrom. They contend that the definition of tannin should be restricted to those substances which irreversibly combine with pelt. They made the valuable discovery that when completely detannized vegetable liquors are evaporated in the presence of air, tannin is generated owing to oxidation and polymerization of organic non-tans present. This is in accord with the findings of Meunier and Seyewitz,[19] that while pure phenols produce only an extremely feeble effect upon the solubility of gelatin, their oxidation products quickly render gelatin insoluble, *e. g.*, hydroquinone has no tanning properties whereas quinone has.

Wilson and Kern showed that this action takes place right in the leather, for when hide powder was drummed in various vegetable extracts and then removed, divided into two portions, one being washed immediately, the other allowed to stand in contact with air for 30 days before washing out the non-tans, the second portion showed in all cases an increased tannin content, thus explaining the importance of the time factor in the "aging" of heavy leather. Alsop's[20] statement, that sole leather tanned slowly not only contains more tannin, but actually consumes less tanning material than rapid tannage, is thus explained.

The knowledge of this chemical change was first made apparent by the introduction and use of the new method of tannin determination invented by Wilson and Kern.[21] This method is radically different from any others previously proposed and used, and as a consequence has met with vigorous opposition although it is based upon sound chemical principles.

The investigators, in a subsequent study[22] of the conduct of quebracho and gambier liquors at different H$^+$-ion concentrations, discovered the interesting fact that at $-\log C_{H^+}=9$, a profound change takes place upon a 24-hr. exposure of these extracts to air, because when brought back to $-\log C_{H^+}=3$, a voluminous precipitate forms. This reaction takes place to a steadily lower extent in solutions more acid than $C_{H^+}=10^{-9}$, but not at all in solutions more alkaline.

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[12] [illegible] 116 [illegible]

[13] *Collegium*, **1920**, 17, 49, 137, 200, 277, 332.

[14] [illegible] 15 [illegible]

[15] [illegible] 109 [illegible]

[16] THIS JOURNAL, **14** [illegible]

[17] THIS JOURNAL, **14** (1922), 292.

[18] *Ibid.*, **12** (1920), 1149.

[19] *Collegium*, **1908**, 195.

[20] *J. Am. Leather Chem. Assoc.*, **15** (1920), 464.

[21] THIS JOURNAL, **12** (1920), 465; **13** (1921), 772.

[22] *Ibid.*, **13** (1921), 1025.

Another point brought out in this paper is the change in color of vegetable extracts with change in H-ion concentration, the color changing from a light straw at $C_{H^+}=10^{-3}$ to a very deep red at 10^{-12}, thus showing that these extracts act like indicators and explaining the long-known fact that the presence of lime in a tanned skin causes darkening of color which brightens if such a skin is treated with acid soon after tanning.

The indicator effect at different H^+-ion concentrations is reversible provided the liquors are not long exposed to air. Upon exposure to air they darken in the more alkaline solutions and the color is not changed back to the original brightness upon reacidification.

SYNTANS

A great deal of attention has been devoted lately to syntans. Although these are not vegetable tannins, however, because of their organic character they should be mentioned here. Syntans are condensation products of formaldehyde with sulfonated cresols and other aromatic compounds. According to Meunier[23] the tanning action of these bodies is due to the free sulfonic and free hydroxyl groups that are absorbed by the skin, thanks to their acid character. If these acid groups are neutralized, the tanning power diminishes. Syntans are now widely used as preliminary tanning agents in the preparation of heavy vegetable leathers, because they cause an increase in the rate of penetration of tannin. Wilson[14] suggests that their chief function is like that which he has described for gallic acid, or the presence of non-tans in permitting tannage in strong liquors without unevenness of fixation.

Moeller[24] points out that syntans cause hydrolysis of hide substance owing to their sulfonic acids, but that such action is materially reduced by the presence of a vegetable extract.

Hill and Merryman[25] insist that while some syntans are useful solely because of their acid character, others really do have tanning action provided they are used under carefully controlled conditions. In combination with vegetable tanning agents, in addition to the increase in rate of penetration, these authors state that syntans produce a tougher and smoother grained leather and have a bleaching action. This latter point is readily understood to be solely a function of their acidity, as demonstrated by Wilson and Kern's[21] experiments.

Hill and Merryman also point out that syntans may be used for deliming and plumping hides for sole leather manufacture. The bating properties of these agents is also discussed by Moeller[26] as a property of the sulfonic acids which they contain. Additional discussion of the uses for syntans along lines just mentioned has been published by Knowles.[27]

The term "synthetic tannins" for the agents considered above is somewhat faulty since they are not synthesized tannins resembling vegetable tannins. Emil Fischer is the only person who has prepared a *bona fide* synthetic tannin, namely, his pentadigalloylglucose. However, the name "syntans" appears to have been firmly established, and for a compact and valuable treatment of these substances the reader is referred to Grasser's new book (translated by Enna).[28]

Grasser[29] has demonstrated that the criterion of gelatin precipitation for a tanning agent is subject to error at times, because hydroxynaphthylmethane sulfonic acid precipitates gelatin but does not tan pelt, while *o*-nitrophenol tans pelt but does not precipitate gelatin.

It has been generally accepted that all tanning agents precipitate gelatin, but, in view of these new cases brought out by Grasser, it appears that actual pelt tests must be made in order to determine whether a new compound has tanning properties.

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[23] *Chimie et industrie*, **1** (1918), 71, 272; *J. Am. Leather Chem. Assoc.*, **13** (1918), 530.

[24] *Collegium*, **1920**, 520.

[25] *J. Am. Leather Chem. Assoc.*, **16** (1921), 484.

[26] *Collegium*, **1921**, 232.

[27] *J. Soc. Leather Trades' Chem.*, **6** (1922), 19.

[28] "Synthetic Tannins," D. Van Nostrand Co., New York, **1922**.

[29] *Collegium*, **1920**, 234.

The Chief Chemist Remarks

A COMPARISON of efficiency of laboratories by two chief chemists led one of them to express himself somewhat as follows:

As a chief chemist, have you ever made a detailed analysis of your men? It has been proved that a man who gets two hundred a month is a better investment for a firm than one who gets one hundred and does only half the work. Do you know who in your laboratory is entitled to a raise? Do you know the weak points of your men? Are you giving them the necessary help? Are you training a man to step into your shoes when the firm gets ready to promote you? Do you give some of your men special work, which could not be given to others who are presumably of the same status? And lastly, are you a better man than your assistants?

To my mind there are ten big factors that make for success in a chemist. These vary with conditions, but for a laboratory worker each is very important: honesty, accuracy, speed, thoroughness, observation, ingenuity, loyalty, personality, health, and education.

They are arranged in the order of their importance. The first three are the most vital and refer to the physical accomplishment of the work. Most young chemists have these points well drilled into them before they leave school. It is unfortunately true that they seem to be the chief and only assets of some chemists.

The next three points are functions of the mind and usually come as the result of experience. It has been said that a man who can make an analysis is worth a hundred dollars; a man who can explain the analysis is worth two hundred dollars; while a man who can interpret and apply the analysis has no limit in value. In most lines of work, thoroughness comes first, but in chemistry, or rather in analytical or research chemistry, it must take the place indicated. The observing man is usually the wide-awake chap who can use waste material to advantage, or suggest a cheaper source of supply. The ingenious man is also the highly paid man—the inventor, or the man who can get out a new product, or cut the cost or time of manufacture.

Loyalty, personality, and health make the leader—the man for whom and with whom you like to work.

The last requirement—education—fills the chinks. It is the most easily obtained, but too often is present as a "trace only."

As an exercise in analysis, try writing these ten points in a column. Beside each point write the name of a man who, to your mind, best represents perfection in that quality. Now check yourself against this column of one hundred per cent men, and finally classify your assistants. You might even plot a curve. By doing this you will soon learn your weaknesses and those of the men working with you.

It is also a good plan to keep a monthly record. This will give you a fairly accurate idea of the men to whom the different types of work should be assigned and of those who deserve a raise. It will also afford an opportunity of checking up the "weak sister;" a heart to heart talk might give him the necessary strength. This plan might also open your own eyes; perhaps you haven't had a raise lately, and perhaps it is because of a bad habit which you have been sheltering.

While these ten points are given for analytical men, very little change will be necessary to make them applicable to any branch of chemistry. For the manufacturing chemist who has not to deal with analyses, but with men, judgment and control might be substituted for accuracy and speed.

Mineral Tannages

By F. L. Seymour-Jones[1]

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AMONG the various mineral tannages that of chrome continues to hold pride of place. Two methods are in general use. In the one-bath process the skins are treated in a solution of a basic chromic salt, usually chrome alum with soda, or bichromate reduced to the chromic state. This is followed by neutralization of the excess of free acid with a suitable weak alkali. In the two-bath process the skins are treated first in a liquor of bichromate and hydrochloric acid, then passed to a reducing bath of acid and sodium thiosulfate. Most of the recent scientific work has been concerned with the one-bath process.

F. L. SEYMOUR-JONES

ONE-BATH CHROME LIQUORS

ACIDITY AND NEUTRAL SALTS—The attainment of a correct basicity is important in the one-bath method. With very basic liquors tannage is extremely slow. With only slightly basic liquors the skins are abnormally plumped by the acid from the salt hydrolysis, and the resulting leather is poor. As the basicity of a chrome liquor is increased a point is reached where the chromium begins to precipitate out. When neutral salts are present in the liquor more alkali is required to bring about incipient precipitation. Wilson and Kern[2] connected this effect with the hydration of the neutral salt in solution. Thomas and Baldwin[3] found no connection between basicity as usually expressed and the true acidity determined with the hydrogen electrode. The acidity of chrome liquors decreases with dilution and with the time of standing. They also found[4] that the addition of chlorides to chromium sulfate solutions invariably increases the hydrion concentration, while sulfates at first decrease it and only increase it again at high concentrations. With sulfuric acid, chlorides increase and sulfates decrease the hydrion concentration. By adding chlorides to chromic chloride solutions Baldwin[5] again found the acidity increased. The addition of neutral salts to chrome liquors was shown by Thomas and Baldwin[6] to give a rapid increase in acidity, followed by a slow decrease. Chlorides increase and sulfates decrease the hydrion concentration of sulfuric and hydrochloric acids. Magnesium sulfate behaves irregularly, decreasing the hydrion concentration up to 0.8 M, but increasing it thereafter. Wilson[7] has shown that for chlorides this effect can be explained by the hydration of the salts in solution, but this cannot hold for sulfates, which decrease acidity. Hence, Thomas and Foster[8] extended this work, using sodium chloride and sulfate, and sucrose, the latter being chosen as a hydrating nonelectrolyte. Since sucrose did not retard tanning except at concentrations greater than 3 M, hydration seems of secondary importance, and they suggest that the chief factor is the formation of addition compounds. Burton[9] earlier considered double salt formation to be of slight importance.

Wilson and Gallun[10] find that the addition of chlorides retards tanning to an extent depending on their concentration. Magnesium chloride is anomalous, the greatest retardation occurring at about molar concentration. Burton and Glover,[11] using gelatin, find that the amount of chromium adsorbed varies with the degree of hydration of the neutral salt; chlorides increase and sulfates decrease the amount of acid taken up. In working on pelt[12] they find that chlorides retard tannage to a greater degree than sulfates. Burton[13] considers that neutral salts in chromium sulfate liquors tend to form acid sulfates. The equilibrium is thus changed and more basic chromium salts are formed with sulfates added than with chlorides.

The work on acidity and neutral salts demonstrates conclusively that difficulties will arise in practice if a chrome liquor is judged solely by its basicity and chromium content. The presence of neutral salts and the age and dilution of the liquor must also be taken into account. Further light on the exact mechanism of these effects is likely to come from a study of chromium salts and solutions from the viewpoint of inorganic, physical, and colloidal chemistry.

CONCENTRATION EFFECTS—The effect of concentration of chrome liquor on the adsorption of its constituents by hide powder has been studied by Baldwin[14] and by Thomas and Kelly.[15] The fixation of chromium by the hide powder rises rapidly to a maximum at a concentration of 1.6 g. of chromic oxide per 100 cc., then falls to a minimum at a concentration of 14.75 g. per 100 cc., at which it remains constant up to 20.2 g. per 100 cc., the limiting value examined. The hydrogen-ion concentration for this was 0.006 M. These figures were obtained by analysis of the tanned powder. If the residual liquor is analyzed, at the higher concentrations "negative adsorption" occurs, *i. e.*, more water than chromic oxide is absorbed. The figures so obtained furnish an interesting example of the danger of determining adsorption by analysis of the residual liquor, a method implying total neglect of the role played by the solvent.

TIME EFFECTS—The effect of varying time on the fixation of chromium by hide powder has been studied over wide ranges of time and concentration by Thomas, Baldwin, and Kelly,[16] and by Thomas and Kelly.[17] Taking 750 as the combining weight of collagen, on the basis of it being the anhydride of gelatin, Wilson[18] points out that for every 100 g. of collagen at least 3.38 g. of chromic oxide are necessarily fixed to produce a chromium collagenate. Thomas, Baldwin and Kelly, plotting concentration of liquor against the amount of chromic oxide fixed by 100 g. of collagen, find sharp maxima, depending on the time but at the same concentration, at amounts of chromic oxide exactly four and eight times 3.38 g., thus pointing to the formation of a tetrachrome and an octachrome collagen. The octachrome curve also shows a point of inflexion, at a higher concentration of liquor, corresponding to a tetrachrome collagen. Even if these results do not definitely prove the formation of a chemical compound, they are of great significance and must be taken into account in any theory of chrome tanning. The work certainly supports the theory of a chemical combination of the chromium and the hide substance.

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[1] [illegible] Fellow of Columbia University 1921-2, 1851 Exhibition Scholar of the University of Leeds.

[2] *J. Am. Leather Chem. Assoc.*, **12** (1917), 445.

[3] *Ibid.*, **13** (1918), 192.

[4] *Ibid.*, **13** [illegible].

[5] *Ibid.*, **14** (1919), 10.

[6] *J. Am. Chem. Soc.*, **41** (1919), [illegible].

[7] *Ibid.*, **42** (1920), 715.

[8] THIS JOURNAL, **14** (1922), 132.

[9] *J. Soc. Leather Trades' Chem.*, **5** (1921), 187.

[10] *J. Am. Leather Chem. Assoc.*, **15** (1920), 273.

[11] *J. Soc. Leather Trades' Chem.*, **5** (1921), 183, 187.

[12] *Ibid.*, **6** (1922), 6.

[13] *Ibid.*, **5** (1921), 192.

[14] *J. Am. Leather Chem. Assoc.*, **14** (1919), 433.

[15] THIS JOURNAL, **13** (1921), 31.

[16] *J. Am. Leather Chem. Assoc.*, **15** (1920), 147.

[17] *Ibid.*, **15** (1920), 487; THIS JOURNAL, **14** (1922), 621.

VIOLET AND GREEN CHROME SOLUTIONS Chromic salts in solution are violet in the cold and green when hot, ordinary solutions being an equilibrium mixture. Two-thirds of the acid radical forms part of the cation in green solution, while in the violet all three chloride ions (in chromic chloride) are anions. The green solutions are far more hydrolyzed, and Blockey[19] showed that in green chrome alum solutions the hydrion concentration is ten times that in the violet. Burton[20] found that violet solutions tan more rapidly than green, which he attributed to the different acidity. Griliches[21] found no difference in the tanning action of green and violet liquors, but his theories of the mechanism of chrome tanning have been severely criticized by Stiasny.[22]

One curious phenomenon in the varying amounts of sodium hydroxide and carbonate necessary to bring about a permanent precipitate in a chrome liquor has been studied by Burton.[23] It is best shown by Burton's figures.

25 CC. 3 PER CENT CHROME ALUM SOLUTION	CC. 0.1 *N* ALKALI REQUIRED TO PRODUCE A PERMANENT PRECIPITATE	
	NaOH	Na_2CO_3
Green	17.8	21.8
Violet	13.2	25.0

That green solutions should require more sodium hydroxide than violet is to be expected in view of their greater acidity, but why the reverse should be true with sodium carbonate is not clear. Burton attributes it to the liberated carbon dioxide functioning as a stabilizing acid in solution, and the more acid green liquors driving more carbon dioxide from solution.

Meunier and Caste[24] with chrome alum solutions found the amounts of sodium carbonate necessary to start precipitation to be proportional to the chromium concentration at 0°, but to increase more rapidly than the chromium concentration at 100°. The amount of soda required decreases on stirring and on heating, due to the liberation of carbon dioxide and the polymerization of basic chrome salts. On aging chrome solutions the amount of soda required at first rapidly increases, then slowly diminishes to a very low value. From old or hot solutions a basic sulfate is precipitated and from fresh or cold solutions, chromium hydroxide.

Burton[25] has recently reviewed the problems of one-bath chrome tanning, and gives an extensive bibliography.

TWO-BATH CHROME LIQUORS

Little work has been done on the two-bath tannage. Innes[26] studied the bleeding of leather from the first (acid-bichromate) bath. He found that most of the chromium which diffuses out is reabsorbed by the skin, and that under certain conditions bleeding is not a serious phenomenon. Schorlemmer[27] points out the disadvantage of even traces of arsenic (0.0015 per cent) in the second (acid-thiosulfate) bath, and advances a theory that the reactions of the second bath are:

$$Na_2S_2O_3 + 2HCl \longrightarrow 2NaCl + H_2SO_3 + S \qquad (1)$$
$$5Na_2S_2O_3 + 6HCl \longrightarrow 2Na_2S_5O_6 + 6NaCl + 3H_2O \qquad (2)$$

Arsenic catalyzes the second reaction, and thus impedes or prevents reduction. This view of the reactions is not in accord with the earlier work of Stiasny and Das,[28] which has met with general acceptance.

MISCELLANEOUS CHROME PROCESSES

Cross, Greenwood, and Lamb[29] have patented the use of concentrated solutions of chrome salts in gum tragasol jellies for rapid tanning, and Turnbull and Carmichael[30] patented starch for the same purpose. While effective and rapid, the process is messy in use, and the jelly material awkward in the drainage channels and pipes. Lamb[31] has patented the use of salts of hydroxy organic acids for stripping chrome leather scraps for glue stock, but this action of such salts in removing chromium from leather (and preventing its proper tannage in chrome liquors) had previously been demonstrated by Procter and Wilson.[32]

THEORY OF CHROME TANNAGE

The theory of chrome tannage is still obscure. Wilson[33] considers that the collagen first combines with a basic chrome salt through a single valence of the chromium atom. Further hydrolysis of the chromium compound then takes place and a second valence of the chromium unites with the collagen. Still more slowly the third valence unites with the collagen, and chromium collagenate is formed. Meunier[34] prefers to regard chrome tanning as a slow and irreversible adsorption of colloidal chromic oxide with the precipitation of a gel on the fibril surfaces, followed by a slow penetration of the gel into the interior of the fibrils.

IRON TANNAGE

Iron tannage is still in the early experimental stage. Pressure of war conditions forced the Germans to adopt it to some extent, and it has met with its greatest application when combined with other tannages, chrome, formaldehyde, and vegetable. Most of the work so far is embodied in the many patents which have been taken out in this connection, particularly by O. Röhm in Germany. Casaburi,[35] and Jackson and Hou[36] have described their work on straight iron tannage and have shown the question of basicity to be of great importance. The keeping qualities of the leather have yet to be demonstrated.

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[18] *J. Am. Leather Chem. Assoc.*, **12** (1917), 108.

[19] *J. Soc. Leather Trades' Chem.*, **2** (1918), 205.

[20] *Ibid.*, **4** (1920), 205.

[21] *Collegium*, **1920**, 416.

[22] *Ibid.*, **1920**, 479.

[23] *J. Soc. Leather Trades' Chem.*, **4** (1920), 205.

[24] *Ibid.*, **5** (1921), 103, 222.

[25] *Ibid.*, **6** (1922), 157.

[26] *J. Soc. Leather Trades' Chem.*, **3** (1919), 104.

[27] *Collegium*, **1921**, 430.

[28] *J. Soc. Chem. Ind.*, **31** (1921), 753.

[29] *J. Soc. Dyers Col.*, **35** (1919), 62.

[30] Brit. Patent 110,470.

[31] Brit. Patent 132,864.

[32] *J. Soc. Chem. Ind.*, **35** (1916), 156.

[33] Private communication; cf. *J. Am. Leather Chem. Assoc.*, **12** (1917), 108, and the theory of alum tanning therein described.

[34] *Chimie et industrie*, **1** (1918), 71, 272.

[35] *J. Soc. Leather Trades' Chem.*, **3** (1919), 61, 74.

[36] *J. Am. Leather Chem. Assoc.*, **16** (1921), 63, 139, 202, 229.

OTHER TANNAGES

Very little scientific work has been done in recent years on tawing (tannage with aluminium salts), or on aldehyde and oil tannages. Moeller[1] has advanced some highly speculative theories based on peptization to account for these, but his work has been severely criticized, and the German technical journals have been occupied with the resulting polemics.

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[1] [illegible] 1918 [illegible] 1919, 61, 72; 1920, 69.

The Preparation of Skin for Tanning

By John Arthur Wilson

CHIEF CHEMIST, A. F. GALLUN & SONS CO., MILWAUKEE, WISCONSIN

JOHN ARTHUR WILSON

THE apparently slow development of the chemistry of leather manufacture has been due to its extreme complexity rather than to any lack of sympathy on the part of practical tanners. This branch of industrial chemistry deals with reactions between those poorly defined groups of substances, usually colloidal, whose compositions are still matters for speculation. The raw skin is composed largely of various kinds of protein matter and is complicated by a structure which varies considerably in different animals and even in different parts of the same skin. Conversion into leather involves the removal of some of these proteins by the action of alkalies, enzymes, or bacteria, and the interaction of the remainder with tanning materials, oils, soaps, emulsions, mordants, dyestuffs, gums, resins, and other complex materials. During these reactions the structure of the skin must be carefully preserved or improved, and highly developed technic is required to impart to the resulting leather certain necessary, but almost indefinable, properties, many of which it is an art even to appreciate fully. When one considers the vast amount of energy expended by organic chemists upon the materials involved in making leather and the uncertainty of our knowledge concerning the individual substances, the complexity of the whole problem becomes more apparent.

HISTOLOGY AND CHEMICAL COMPOSITION OF SKIN

Scientific investigations in the preparation of skin for tanning have been retarded by insufficient knowledge of the histology and chemical composition of the skins of the lower animals which have structures very different from human skin. The need has been well appreciated, but very few leather chemists have had the time, facilities, or technic required to obtain the desired information.

Recently, however, the literature on the histology of skin has been greatly enhanced by a valuable series of articles published by Alfred Seymour-Jones.[1] In addition, studies have been in progress in the writer's laboratories during the past four years of the microscopic structure of the skins of the lower animals and the changes undergone during their conversion into leather. Part of this work has already been presented and its scope is gradually being extended. The importance of such studies warrants their becoming more widespread.

A review of the literature on the chemical constituents of skin has recently been made by F. L. Seymour-Jones.[3] The difficulty in making quantitative separations of the protein constituents of skin makes this type of study even more difficult than that of histology.

Many of our conceptions of the physical chemistry of the skin proteins have been derived from investigations on gelatin, particularly those of Procter[4] and his collaborators,[5] and of Jacques Loeb.[6] Loeb's work is a splendid example of the common interest which all branches of the science have in fundamental research. Although performed for its value to physiology, it has proved of great importance to leather chemistry.

PRESERVATION AND DISINFECTION OF SKIN

Raw skins are highly putrescible, and it is necessary to preserve them in some way until the first tanning operation. This is usually done by saturating with common salt, or by drying.

The attention of chemists has frequently been drawn to the appearance of stains on salted skins, usually called salt stains because their frequency of occurrence was found to be influenced by the composition of salt used and the method of its application. The staining is apparently due to a combination of the skin proteins with iron, derived either from the skin itself or from the added salt. In their natural state the iron compounds of the skin are incapable of staining, but assume this power if rendered soluble by bacterial or purely chemical action.

J. Paessler[7] found that the percentage of stains could be greatly reduced by using salt containing 3 per cent of its weight of anhydrous sodium carbonate. This retarded bacterial action prevented iron from passing into solution and served as a denaturant, in place of some more harmful material, in those countries of Europe where edible salt is taxed and salt for industrial purposes must be denatured. Abt,[8] finding some bad cases of staining were due to calcium sulfate in the salt used, pictured the reactions as follows:

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[1] [illegible] J. Am. Leather Chem. Assoc., 1917–21 [illegible]

[2] [illegible] presented at the 62nd Meeting of the American Chemical Society, New York, N. Y., September 9, 1921, publication, including numerous photomicrographs, reserved for the Society's monograph on "The Chemistry of Leather Manufacture."

[3] THIS JOURNAL, **14** (1922), 130.

[4] *J. Chem. Soc.*, **105** (1914), 313; **109** (1916), 307.

[5] *J. Am. Chem. Soc.*, **40** (1918), 886.

[6] *J. General Physiol.*, **1918–22**; "Proteins and the Theory of Colloidal Behavior," McGraw-Hill, **1922**.

[7] "Salting of Hides and Skins," *Ledertechnischen Rundschau*, **1912**, 137.

[8] "Microscopical Examination of Skin and Leather Applied to the Study of Salt Stains," *Collegium*, **1914**, 130.

The calcium sulfate reacted with ammonium phosphate from the nucleic acids of the skin, precipitating calcium phosphate; the ammonium sulfate thus formed rendered soluble the ferrous carbonate naturally occurring in the skin, which in turn combined with the skin, forming a stain. Becker[9] showed that the stains could be produced by pure cultures of bacteria isolated from the stains. Romana and Baldracco[10] prevented the stains by adding sodium fluoride to the salt or by washing the lymph, containing much of the iron, out of the skins immediately after flaying, but before salting.

Dried skins often come from regions infected with certain disease germs, of which anthrax is the one most dreaded. Such skins must be disinfected and apparently the best method devised is that of Alfred Seymour-Jones,[11] which consists of soaking the dried skins for from 1 to 3 days in a solution of 1 per cent of formic acid and 0.02 per cent of mercuric chloride, followed by immersion in a saturated salt solution for an hour, draining and baling for shipment. Both Abt and Seymour-Jones have pointed out, however, that hides would contain no anthrax if dried in the sun immediately after flaying.

Changes begin to take place in the skin immediately after the death of the animal. McLaughlin[12] recently found that the degree of swelling of hide in limewater depends upon the time lapse since the death of the animal. As for the practical significance of this fact, the writer has put into process together both properly preserved skins and skins taken from animals within an hour after death and could detect no difference in the finished leathers by microscopical, chemical, and physical analysis.

Soaking and Fleshing

Among the first tannery operations are washing to remove blood and lymph, soaking in cold water for several days to swell the fibers and bring them again into equilibrium with water, and the removal of the adipose tissue or flesh. The contribution of chemists in the soaking operation has been in the direction of hastening the absorption of water, in the case of dried skins, by the addition of acids or alkalies under proper control. The reason why skins must be completely wet back before fleshing or tanning is prettily illustrated in a paper on gelatin by Sheppard and Elliott.[13] Cubes and cylinders of gelatin jelly always suffer a change of shape during drying because of the greater initial rate of drying and casehardening of the edges. Skins fleshed without sufficient preliminary soaking will look smooth on the flesh side upon coming from the fleshing machine, but later, when the skin has absorbed more water, the flesh side will be so ragged and uneven as to require further treatment. If dried skins are not completely soaked back before entering the tan liquors, the distortions suffered by the fibers during the original drying will be permanently fixed by the tanning action and the leather will never have the proper suppleness.

Unhairing

Recent microscopical studies have demonstrated clearly that the loosening of the hair and epidermis by the common methods of liming and sweating, as well as by the newer methods involving enzyme action, is due to the digestion of the cell walls of the Malpighian layer of the epidermis resting on the true skin, the destruction of which leaves the hair and epidermis completely separated from the rest of the skin.

Since sterile limewater has little unhairing action on skins, it was long thought that bacteria were necessary for this action. But Schlichte[14] found that skin previously sterilized by the Seymour-Jones process could be unhaired easily after two weeks of contact with saturated limewater under sterile conditions. Wood and Law,[15] however, pointed out that the action may have been influenced by the previous swelling of the skin in the sterilizing solution. This action of swelling agents in making protein matter more susceptible to hydrolysis is now receiving increased attention.

Röhm[16] devised a process for unhairing by means of an alkaline trypsin solution. In describing Röhm's process, Hollander[17] pointed out that a skin can be unhaired by soaking for one day in a dilute solution of sodium hydroxide and then for one day in a solution of sodium bicarbonate to which trypsin is added after the swelling of the skin has been counteracted. In the discussion following Röhm's presentation of his paper, Eberle expressed doubt that the hair loosening was due to the enzyme. In a recent investigation, Wilson and Gallun[18] confirmed Hollander's findings and showed that the action proceeds slowly in the absence of the enzyme, but is greatly accelerated by its presence and by rise of temperature up to 40°; but, when the experiments were conducted under toluene to check bacterial action, there was no unhairing action at 25°, but a very marked action at 40°, indicating that pancreatin is an unhairing agent at 40° but that the action obtained at lower temperatures in practice is due to something other than pancreatin.

Ross[19] patented a process for unhairing with thrombase naturally occurring in skin. If proved sound, his view will be an important addition to our knowledge of the action of old lime liquors. J. T. Wood,[20] of Nottingham, found that formic acid will unhair a skin if sufficient time is allowed. The subject of acid unhairing has since been reviewed by Marriott.[21] Apparently anything that will hydrolyze the newly formed cells of the epidermis without injuring the rest of the skin is a satisfactory unhairing agent.

The extent to which the unhairing agent swells the skin has an important effect on the appearance of the finished leather, excessive swelling tending to produce a roughness of the grain surface. Atkin[22] was able to reason from the theories of Procter, Wilson, and Loeb[23] that the addition of arsenic disulfide to a lime liquor should cause less swelling than the addition of sodium sulfide and thus leave the skin with a finer grain surface. His reasoning is borne out in practice in the case of glazed kid leathers.

Bating

One of the greatest blessings which the industry has derived from chemistry is the replacement of the obnoxious dungs formerly used in bating by pancreatic enzymes. After liming, unhairing, and washing the skins, it was customary to put them into warm infusions of the dung of dogs or fowls until they had become very soft and flaccid. The dung appeared to be necessary to remove some undesirable constituent of the skin until Wood,[24] in 1898, discovered that the same action could be obtained by pancreatin under suitable

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[9] "Salt Stains," *Collegium*, **1912**, 408.

[10] "Salting of Hides and Avoidance of Salt Stains," *Collegium*, **1912**, 533.

[11] "Formic-Mercury Anthrax Sterilization Method," London, **1910**; "Anthrax Prophylaxis in the Leather Industry," *J. Am. Leather Chem. Assoc.*, **17** (1922), 55.

[12] *J. Am. Leather Chem. Assoc.*, **16** (1921), 435.

[13] *J. Am. Chem. Soc.*, **44** (1922), 373.

[14] *J. Am. Leather Chem. Assoc.*, **10** (1915), 585.

[15] *J. Soc. Chem. Ind.*, **35** (1916), 585.

[16] *Collegium*, **1913**, 374.

[17] *J. Am. Leather Chem. Assoc.*, **15** (1920), 477.

[18] "Pancreatin as an Unhairing Agent" (not yet published).

[19] Brit. Patent 169,730; cf. *C. A.*, **16** (1922), 853.

[20] Private communication to writer in 1916; *J. Am. Leather Chem. Assoc.*, **12** (1917), 114.

[21] *J. Soc. Leather Trades' Chem.*, **5** (1921), 2.

[22] THIS JOURNAL, **14** (1922), 412.

[23] *Loc. cit.*

[24] "Puering, Bating, and Drenching of Skins," E. and F. N. Spon, London.

[illegible] was removed, however. [illegible] Rosenthal[illegible] found that the material removed was a protein, and assumed that it was [illegible] in collaboration with Wood, studied the effect of bating with pancreatin and concluded that bating dissolves the elastin fibers of the grain membrane. Wilson and Daub[27] examined the bating action under the microscope and showed unmistakably that the elastin fibers were dissolved away completely by the action of pancreatin. They then made an exhaustive study of the rate of digestion of elastin fibers from calfskin as a function of concentration of enzyme and ammonium chloride, time, and pH value, which has reduced the control of this operation from one of the most difficult to one of the simplest in the tannery.

The empirical method for determining the completion of the bating process is by noting when the swelling or plumping of the skin has been entirely counteracted and the skin is quite flaccid. Wilson and Daub observed a point of minimum plumping at a pH value of about 8. But Thomas and Kelly[28] and Porter[29] found the isoelectric point of collagen to be at about pH = 5. More recently Wilson and Gallun[30] made a careful study of the plumping of unhaired calfskin as a function of pH value and found two points of minimum, one near 5 and the other near 8, the one near 5 having the lower value. This seems to indicate that what we call collagen consists of a mixture of proteins of very different isoelectric point, or else that collagen undergoes some internal change, possibly tautomeric, with change of pH value that tends to shift its isoelectric point.

It has generally been thought that pancreatin is practically without action upon collagen. In fact Wilson and Daub could detect no appreciable destruction of collagen under the microscope while observing the complete solution of elastin. But F. L. Seymour-Jones,[31] experimenting upon hide powder, has found that under the right conditions and with sufficient quantity of enzyme, collagen is easily attacked and dissolved by pancreatin. Wilson and Gallun have found that pancreatin will dissolve calfskin if given sufficient time. In one experiment they found no visible destruction of collagen for the first 24 hrs., but during the second day the fibers began to dissolve comparatively very rapidly, suggesting that the fibers possess a very thin surface much more resistant to tryptic digestion than the substance in the interior. The action of enzymes on skin during its preparation for tanning offers a fertile field for further research.

[illegible] 11 (1916), [illegible]

[illegible] J. Soc. Leather Trades' Chem., 4 (1920), 60.

[illegible] 12 [illegible] 13 (1921) [illegible]

[illegible] J. Am. Chem. Soc., 44 (1922), 195.

[illegible] J. Am. Leather Chem. Assoc., 5 (1921), [illegible]

[illegible] "Plumping of Calfskin," not yet published.

[illegible]

[illegible] appointment of second lieutenants in the [illegible] will be held the week beginning October 2[illegible], [illegible] will be tendered successful candidates [illegible] December 31, 1922 in the following [illegible] Field Artillery, Coast Artillery, [illegible] Signal Corps, Quartermaster [illegible] Chemical Warfare Service, Finance Department, and Philippine Scouts. Applicants must [illegible] the [illegible] 21 and [illegible] years. Each candidate is permitted to express his first and second [illegible] post.

Rare Organic Chemicals

By H. T. Clarke

Eastman Kodak Co., Rochester, N. Y.

By "rare organic chemicals" is here understood chemicals required in relatively small quantities exclusively for laboratory purposes, whether for chemical research, analytical work, or experimentation in medical or physical science. Certain of the chemicals employed in pharmacy, perfuming, flavoring, and other industries might reasonably be classed under this head; but in this article the above definition will be followed, to the exclusion of all industrial products.

H. T. Clarke

The history of the progress of the manufacture of this class of chemicals in the United States really dates from eight years ago, when the supply from Germany ceased. Before that time practically nothing of the sort was made in this country, American chemists being content to draw their requirements, either directly or through supply houses, from the two important German firms which between them had built up the source from which the needs of the entire world were filled. When the pinch came, practically nothing was done during the first three years to relieve the situation, since the attention of chemical manufacturers was necessarily directed to more urgent, at any rate more spectacular, problems. The first step was taken in 1916 in the University of Illinois, when Prof. C. G. Derick inaugurated a vacation class in which, under his direction, the otherwise inaccessible organic chemicals required during the coming year were prepared. This valuable work, which did not excite imitation in other universities,[1] was continued in the same laboratory by Prof. Roger Adams, who was able to supply a certain proportion of the products of the Illinois laboratory to other universities. It was not until the latter part of 1918 that commercial firms began to enter the field. The first of these was the Eastman Kodak Co., whose action was followed by a number of concerns, in particular the Heyl Laboratories, the Special Chemicals Co., and the Synthetic Laboratories of Chicago, organized for the specific purpose of manufacturing research organic chemicals.

The success of these undertakings has of course depended largely on the coöperation of the manufacturers of those organic chemicals that are employed on a larger scale, and this has in all cases been cordially and generously accorded. Manufacturers of crudes, intermediates, and dyes, such as The Barrett Co., E. I. duPont de Nemours & Co., The National Aniline & Chemical Co., the Calco Chemical Co., The Dow Chemical Co., The Monsanto Chemical Works, The Sherwin-Williams Co., to mention but a few of the more

[1] An exception should be made in the case of the University of Wisconsin in which a considerable amount of time has more recently been devoted to the preparation of chemicals for its own use.

important, have continually furnished information as to the products they manufacture not only for sale but for their own use. The same has been the case with the firms manufacturing pharmaceuticals, perfumes, and flavoring chemicals. Some of these concerns have indeed contributed nobly by putting in the market, often without financial profit, lines of pure organic chemicals for research and development purposes. This has been done by the U. S. Industrial Chemical Co. (pure alcohols and esters), the Fries & Fries Co. (pure acids and esters), the Digestive Ferments Co. (rare sugars for bacteriology), and the General Motors Research Corporation (hydroaromatic compounds).

Valuable work has also been done by certain firms who have made readily available certain compounds that had hitherto been classed as "rare chemicals." Thus, The Dow Chemical Company now produces pure ethylene glycol, ethylene chlorohydrin and its acetate, and dichloroacetic acid; the Standard Oil Company and Carbide & Carbon Chemicals Corporation have rendered isopropyl alcohol as accessible a solvent as ethyl alcohol; while the Hirsch Laboratories have placed on the market a series of aliphatic amines and their derivatives.

With regard to the avowedly rare, and therefore generally expensive, organic chemicals, the greatest number have been prepared in the Research Laboratory of the Eastman Kodak Co., who now have a list of over 1300 different chemicals. No attempt has been made to develop any special line, for the object has been to prepare only those chemicals that are not produced commercially on a technical scale, and to build up as long a series of rare organic chemicals in as short a time as possible. During the past 12 mo., 253 new chemicals have been added to the list, of which 187 were prepared in the Eastman Kodak Laboratories. The remaining 26 per cent can be accounted for principally by the growth of the range of organic chemicals produced technically. It is interesting to note in this connection that the list of Kahlbaum contains the names of just over 2000 organic chemicals, so that to reach this number not much more than three years more should be necessary. There can be little doubt, moreover, that the manufacturers of rare organic chemicals in Germany are (or were) able to draw upon a much wider group of commercial chemicals than has yet been possible in the United States; this would explain the occasional startling differences in price between certain German chemicals and the same products listed as rare chemicals in this country.

One of the most spectacular fields of rare organic chemicals is occupied by the sugar family. The production of these compounds constitutes almost a special branch of chemistry in itself, and there are few organic chemists who would dare to enter this field without special preparation. American chemists and bacteriologists are thus greatly indebted to the Digestive Ferments Company and to the Special Chemicals Company for their fine work in making available an extensive list of the uncommon sugars in pure form. The amount of skill and labor necessary for their preparation and the urgency with which they are required for special work may be estimated from their cost, which in certain instances amounts to several dollars per gram. An allied field is represented in the amino acids required for bacteriological and physiological research. Here again valuable services have been rendered by the Special Chemicals Company and the Abbott Laboratories, as well as by certain private workers, notably Mr. H. J. Bean, who has specialized in physiological-chemical reagents of the meticulous degree of purity required for such work.

Another highly technical branch of chemistry which has collaborated with the medical sciences is the production of bacteriological and medicinal dyes, an alliance which, while already extensive, is apparently still in the infancy of its possibilities. The admirable work carried out by the Heyl Laboratories—now incorporated with the National Aniline & Chemical Company—constitutes an almost unique achievement in this domain, the quality of their products surpassing those of the European laboratories.

Closely related are the indicators employed in the modern methods involving hydrogen-ion concentration. The works of Clark and Lubs, of Acree, and of Walpole have demonstrated the great value of the sulfonphthalein family of indicators (which, by the way, are also employed in experimental medicine), and this series of dyes has been well taken care of by the Pyrolectric Instrument Co., The Coleman and Bell Co., Hynson, Westcott and Dunning, and LaMotte Chemical Products Co., all of which also manufacture the more important of the other indicators.

It is difficult for the average chemist in his laboratory to keep himself informed of the various products that are available; and to assist such workers a list of American Research Chemicals has been prepared under the auspices of the National Research Council by Dr. Clarence J. West. It would be difficult to exaggerate the value of this list, which is published annually and contains the name of every available chemical, together with an index number for the firms from which it can be obtained. Dr. West certainly deserves the gratitude of every chemist for the admirable way in which he has discharged his laborious task.

Publicity is also being given to methods for the preparation of a number of rare organic chemicals. In the organic chemical manufactures of the University of Illinois, to which reference was made above, a number of chemical reactions are studied, and reports of these have been published annually in the University of Illinois Bulletin by Roger Adams, O. Kamm, and C. S. Marvel. The information contained therein is of great value to all chemists engaged in organic research work. Another series of annual publications, also stimulated into existence by Dr. Roger Adams, dealing with the preparation of organic chemicals, is that entitled "Organic Syntheses" (John Wiley & Sons). This is a more elaborate work, in which each of the preparations described has been drawn up so as to leave no possibility of doubt and mistake in procedure, and has been carefully checked by a member of the editorial board.

The Public Health Institute of Chicago has undertaken to finance the coöperative research between the University of Wisconsin Medical School and the Chemical Department of Northwestern University, which in the past has been supported by appropriations from the U. S. Interdepartmental Social Hygiene Board. This research, which has been devoted to attempts to improve the treatment of syphilis of the central nervous system, has been directed by Dr. W. Lee Lewis and Dr. F. C. Whitmore of Northwestern University, and Dr. A. S. Loevenhart and Dr. W. F. Lorenz of the University of Wisconsin. The Public Health Institute has appropriated $21,600 for the use of both universities during the coming year.

A series of lectures on the Geology of Commerce and Industry is to be given by Dr. Ernest R. Lilley at the School of Commerce, New York University. During the fall term the commercial geology of the fuels, chemicals, and building materials will be discussed in a nontechnical manner, covering for each of the basic commodities the properties and uses, methods of exploitation and conservation, including mining and preparation for market, and the relation between market prices and production costs. During the spring term the lecturer will treat the commercial geology of the metals, dividing the subject as follows: the iron group, the nonferrous metal group, the precious metals, and the process minerals. Stress will be laid upon the nature and cost of smelting and refining.

Organic Catalysis

By E. Emmet Reid

Johns Hopkins University, Baltimore, Maryland

THE PAST year has seen much activity in the study of the mechanism of catalysis and a more exact study of the influence of the precise method of preparation of a catalyst on its activities, both qualitatively and quantitatively. The most striking contributions to the literature are briefly summarized in the following paragraphs.

E. Emmet Reid

The mechanism of catalysis has been studied by Langmuir.[1] Taylor and Burns[2] lay a foundation for reasoning and calculating by measuring the adsorption of hydrogen, carbon monoxide, carbon dioxide, and ethylene by nickel, cobalt, iron, platinum, and palladium. They find that adsorption is specific and that saturation is reached at low pressures. Preparations of the metals which are good absorbers are good catalysts.

Palmer and Palmer[3] make an intensive study of the hydrogenation of ethylene and explain all their results in terms of the absorption of hydrogen or ethylene on the surface of the nickel. At first the metal is covered with hydrogen and the reaction is slow. Some of this is driven off by the heat of the reaction and ethylene condenses on a part of the surface. This is the condition of maximum efficiency and the reaction slows up when too much ethylene chokes up the surface.

Rideal[4] can find no period of induction except when oxygen is present. He adopts Langmuir's view that the metal is covered with a film of hydrogen and ethylene one molecule deep and that the reaction is between the ethylene and hydrogen molecules that find themselves adjacent in this film.

Maxted[5] makes a quantitative study of the influence of poisons, lead, mercury, sulfur, and zinc, on the occlusion of hydrogen by palladium and on the catalytic power of platinum and palladium. The rate at which hydrogen is taken up is affected far more than the amount, two weeks being required for saturation with 19 per cent of lead on the palladium. With 17 per cent of lead the amount of hydrogen absorbed is reduced only 50 per cent while the rate of hydrogenation is decreased 98 per cent, which indicates that the catalytic action is confined to the surface. To cut the catalytic activity of platinum in half requires 10 per cent mercury or sulfur and only 4 per cent arsenic or zinc.

Armstrong and Hilditch[6] study the relation between the pressure of the hydrogen and the rate of hydrogenation. It appears that H_2 rather than H is the reactant, the rate being directly proportional to the pressure, provided at least 0.1 per cent nickel is present. With 0.01 per cent, the rate is too low, which seems to show that a part of the metal is combined with the ethylene groups.

Rideal[7] makes a valuable addition to our scanty quantitative data on hydrogenation by determining the dissociation pressures of the hydrogen from ethyl and isopropyl alcohols between 105° and 275° over a copper catalyst.

Matignon[8] and Herzfeld consider the formation of intermediate compounds from the standpoint of thermodynamics.

Dhar and Mittra[9] find that the oxidation of a more oxidizable substance is slowed down in the presence of the substance in which it induces oxidation. The second substance may be considered a negative catalyst. The explanation may be found in the formation of complexes.

Burrows[10] finds that the addition of sucrose, which is itself hydrolyzed, slightly accelerates the hydrolysis of methyl acetate by hydrochloric acid.

Sherman and co-workers[11] measure the influence of amino acids, copper salts, etc., on the activity of amylases.

Coffey[12] upsets tradition by showing that, under the influence of driers, oils take up only 0.6 as much oxygen as without.

Taylor and Lewis[13] study the absorption spectra of triethyl sulfonium bromide in eight solvents in an attempt to find a connection between reactions and light absorption. Most of the absorption bands were in the calculated positions.

Baly, Heilbron, and Barker[14] effect the photosynthesis of formaldehyde from carbon dioxide in water illuminated by light of short wave length, $\lambda = 200\ \mu\mu$. The formaldehyde passes into reducing sugars in light of $\lambda = 290\ \mu\mu$. In the presence of certain colored substances, the photosynthesis takes place under the influence of visible light.

Schwarz and Friedrich[15] find that Röntgen rays poison a platinum catalyst.

Rosenmund and Zetzsche[16] have made an extensive study of stopping reactions at the desired place. The following reactions occur by catalytic hydrogenation: benzoyl chloride ⟶ benzaldehyde ⟶ benzyl alcohol ⟶ toluene. By adding a trace of sulfurized quinoline, 88 per cent aldehyde can be obtained.

Adkins and Krause[17] conclude that the method of preparation of a catalyst is of equal, if not greater, importance than the particular metallic element present.

Willstätter and Waldschmidt-Leitz[18] claim that hydrogenation cannot be effected with platinum or palladium free from oxygen, and suggest that catalytic poisons remove this all-important oxygen. Their experiments appear exact and convincing. H. S. Taylor explains their results by assuming that a catalyst may so cover itself up with hydrogen that the substance to be reduced cannot get to it. Kelber[19] flatly contradicts their results so far as nickel catalyst is concerned, finding that nickel is active in the absence of oxygen and may be killed by air even at −20°, but can be revivified by treatment with hydrogen at 70° to 80°. Skita[20] took pains to exclude oxygen from the catalyst and all reactants and yet obtained rapid hydrogenations with platinum. Voorhees and Adams[21] agree that oxygen is necessary with a platinum catalyst. They simplify and improve the preparation of platinum black.

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[1] [illegible], **16** (1922), 864.

[2] [illegible], **43** (1921), 1273.

[3] [illegible] 99A [illegible]

[4] [illegible] 121 [illegible]

[5] [illegible] 119 [illegible]

[6] [illegible] 100A [illegible]

[7] [illegible] 99A [illegible]

[8] *Chim. et industrie*, **6** (1921), 7; *Z. phys. Chem.*, **98** (1921), 161.

[9] *Chem. News*, **123** (1921), 313.

[10] *J. Chem. Soc.*, **119** (1921), 1798.

[11] *J. Am. Chem. Soc.*, **43** (1921), 2454, 2461, 2469.

[12] *J. Chem. Soc.*, **121** (1922), 17.

[13] *Ibid.*, **121** (1921), 665.

[14] *Ibid.*, **119** (1921), 1025.

[15] *Ber.*, **55** (1922), 1040.

[16] *Ibid.*, **54** (1921), 425, 638, 1092, 2033, 2038; **55** (1922), 609; Abel, *Ibid.*, **54** (1921), 1407; **55** (1922), 322.

[17] *J. Am. Chem. Soc.*, **44** (1922), 385.

[18] *Ber.*, **54** (1921), 113.

Cake[22] opens up an important field by hydrogenating glucose to *d*-sorbitol and *d*-mannitol.

Milligan and Reid[23] transfer hydrogen from an alcohol to an aldehyde.

Mailhe[24] eliminates halogens catalytically and[25] prepares cyclohexylamine by hydrogenating cyclohexanone hydrazone.

Brand and Steiner[26] hydrogenate aromatic nitro compounds to β-aryl-hydroxylamines or to azoxy and hydrazo compounds.

Schroeter[27] gives details of the preparation of tetralin and elaborates the chemistry of a multitude of its substitution products.

Wieland[28] lines up catalytic oxidation with hydrogenation by holding that the hydrogen of the compound is activated and made to combine with oxygen; what we usually call an oxidizing agent is really only an acceptor for the activated hydrogen.

Karczag[29] compares the speed of oxidation of 34 dyes by hydrogen peroxide in the presence of salts of iron, copper, nickel, manganese cobalt, and platinum. A ferrous salt acts faster than a ferric.

Clover[30] finds the autoxidation of ether to be hastened by acetaldehyde.

Conover and Gibbs[31] describe the oxidation of naphthalene by air over vanadium pentoxide at 400° to 500°. They list many other catalysts which can be used, but with poorer results. This has become an important commercial process.

Scholl and co-workers[32] have found that aluminium chloride greatly facilitates the removal of hydrogen from aromatic rings, whereby two nuclei are united as in the formation of diphenyl from benzene. With this catalyst the reaction may go well at 100° to 150°, so that products may be obtained that are otherwise out of the question. They synthesize perylene, benzanthrone, 4.5, 8.9-dibenz-pyrenequinone, 3,10, etc.

More along the usual Friedel and Crafts lines, Smith,[33] Stephens and McMullen have prepared a number of new benzoyl benzoic acids. Milligan and Reid[34] have ethylated benzene and naphthalene with ethylene, the reaction being hastened enormously by high-speed stirring. Korczynski and Mrszinski[35] find that chlorides of cobalt, nickel, iron, and tungsten may be used instead of copper chloride with aluminium chloride to effect the synthesis of aromatic aldehydes from carbon monoxide.

Gilfillan[36] compares the dehydrating power of silica, thoria, titania, and blue oxide of tungsten, on alcohols.

Vogt and Nieuwland[37] study the most effective form of mercury for catalyzing the synthesis of acetaldehyde.

Mailhe and de Godon[38] alkylate aniline by the aid of alumina.

[19] *Ber.*, **54** (1921), 1701.
[20] *Ibid.*, **55** (1922), 139.
[21] *J. Am. Chem. Soc.*, **44** (1922), 1397.
[22] *Ibid.*, **44** (1922), 859.
[23] *Ibid.*, **44** (1922), 202.
[24] *Bull. soc. chim.* (*Paris*), [4] **29** (1922), 535.
[25] *Compt. rend.*, **174** (1922), 465.
[26] *Ber.*, **55** (1922), 875.
[27] *Ann.*, **426** (1922), 1.
[28] *Ber.*, **54** (1921), 2353.
[29] *Biochem. Z.*, **117** (1921), 69.
[30] *J. Am. Chem. Soc.*, **44** (1922), 1109.
[31] THIS JOURNAL, **14** (1922), 120.
[32] *Ber.*, **55** (1922), 109, 118, 324, 330.
[33] *J. Am. Chem. Soc.*, **43** (1921), 1920; *Ibid.*, **43** (1921), 1950; *Ibid.*, **43** (1921), 1965.
[34] *Ibid.*, **44** (1922), 206.
[35] *Bull. soc. chim.* (*Paris*), [4] **29** (1921), 459.
[36] *J. Am. Chem. Soc.*, **44** (1922), 1323.
[37] *Ibid.*, **43** (1921), 2071.
[38] *Compt. rend.*, **172** (1921), 1417.

Oil-Cracking Patent Application of 1913 Just Granted

At the present time much gasoline is made by "cracking," which is the oil man's alias for destructive distillation. Oil is heated until it breaks down and one of the products is gasoline. A chemical process of making gasoline is described in the McAfee patent on "Process of Converting Oil," No. 1,424,574, issued to the Gulf Refining Company, August 1, 1922, on an application which has been on file in the Patent Office since 1913. Mr. McAfee says that he can make sweet saturated gasoline from higher boiling oils, such as gas oil or fuel oil, with the aid of anhydrous aluminium chloride at temperatures considerably below cracking temperatures and without the breaking down or destruction incident to cracking. The high boiling oil is heated in the presence of anhydrous aluminium chloride to a temperature corresponding to the boiling point of the mixture, and for a clean separation only the vapors at about 350° F. or less are allowed to go to the final condenser, while all vapors at a higher temperature are recondensed and returned to the condensing still. This insures returning to the still vaporized aluminium chloride and prevents it from condensing with the final gasoline formed.

In the Patent Office the progress of Mr. McAfee's application to patent was delayed by legal proceedings incident to an "interference." The contest was between Mr. McAfee and another chemist, employed by one of the large oil companies; but after protracted litigation in the Patent Office and before the Court of Appeals of the District of Columbia, Mr. McAfee was finally adjudged the inventor.

It is stated that the Gulf Refining Company has been making gasoline by the patented method for several years with entirely satisfactory results. The initial and the end boiling points of the produced gasoline can be limited within a narrow range and the material is of sweet saturated nature. The high temperatures and high pressures of the usual cracking methods are not used. The gasoline made by this aluminium chloride process, being saturated, shows practically no iodine number or heat reaction with sulfuric acid and is thus distinguished from the cracked gasolines.

The low boiling hydrocarbons found in gasoline are less complex chemically than the hydrocarbons of high boiling oils. The new process therefore contradistinguishes from various well-known building-up actions exerted by aluminium chloride by which more complex are made from less complex hydrocarbons. The elimination of building-up action in the Gulf process seems to be connected with the continual return of volatilized aluminium chloride to the still and the constant removal of gasoline as it is formed, leaving only high boiling oils to be acted on by the catalyst. The net result is the production of very little gas or high boiling material, with yields of commercial gasoline as high as 85 per cent of the original oil.

The aluminium chloride seems to act as a simple catalyst in the conversion process, since its period of utility is limited only by the carbon and heavy oils with which it combines after a rather long use. When this happens, the aluminium chloride can be revived for re-use by a process which also is patented by the Gulf Refining Company.

The Gulf Refining Company is said to be willing to license oil companies under the patented process and several improvement patents, including the so-called "recovery process" and certain patents covering inexpensive methods of manufacturing anhydrous aluminium chloride.

A meeting of representatives of various dyeing and bleaching concerns in Pennsylvania, New York, Massachusetts, and Rhode Island was held at the Hotel Biltmore, New York, N. Y., on June 21, 1922, for the purpose of considering the advisability of the formation of a national organization of dyers and bleachers.

Chemistry of Sanitation

By **A. M. Buswell**

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[illegible] of Potable Water

WITH THE development of quantitative bacteriological technic, chemical tests for determining the sanitary quality of water lost much of their former importance. Because of increasing necessity for the use of surface supplies, all of which are more or less subject to pollution, the main question has become one of purification rather than of a test for freedom from infection, and it should be remembered that purification involves a great deal more than disinfection. Disease germs can be killed or got rid of with comparative ease, but tastes, odors, and turbidity must also be removed in order to produce a potable water.

A. M. Buswell

Water purification is, therefore, an essential chemical process and it is along the line of the investigations of the reactions involved and methods for their control that the water chemist is again coming into his own. Though it is possible at the present time to produce a potable water from almost any source, no matter how polluted, yet there is room for improvement of the product as well as of the process. Furthermore, the art is at present ahead of the theory. We can purify water with reasonable success, but we do not understand the mechanism of the reactions involved. "Who but the chemist is to fix the proper value for the dose of chemicals?" said Professor Mason[1,*] seven years ago, and we might add, "Who but the chemist can investigate the complicated reactions of these chemicals?"

The following steps represent what may fairly be considered as present standard practice in purification of municipal surface supplies for general domestic use: coagulation with aluminium sulfate or ferrous sulfate; sedimentation; rapid filtration through sand; and, finally, disinfection with chlorine. Some of the earlier "slow sand" filters are still in use, especially in Europe. In some cases chlorination without filtration is used as a more or less temporary measure and in a few instances filtration without chlorination is regarded as sufficient. Softening or iron removal is sometimes attempted, but in general such treatment is left to the private or industrial consumers.

The relation of pH to precipitation of $Al(OH)_3$ has probably been the most extensively investigated problem in the last few years. Practice had been to add lime to waters which [illegible] 20 p. p. m. [illegible] Wolman and Hannan[2] showed [illegible] in most cases but that in some instances the addition of small amounts [illegible]. At the same time Buswell and Greenfield[3] investigated the various reactions of water [illegible] the [illegible] the American Water Works Association, R. S. Weston, chairman, with the aid of a number of filter plant operators, compiled this year a considerable amount of data which will be published in the journal of that society. Clark and Theriault[3] report that hydrogen electrode experiments have shown that equilibria in aluminium solutions with the solid phase (aluminium hydroxide?) present are complex. The peculiarities nullify the value of methods previously used to estimate the isoelectric point. By taking advantage of these peculiarities the isoelectric point has been found to lie between pH 5.5 and 6.0. Experiments on time of flocculation have shown minimum time at or near pH 5.5. An empirical equation has been found relating time for first appearance of floc and pH under uniform sets of laboratory conditions. Time of flocculation is also a function of circulation, and rough relations have been found whereby small vessel experiments may be extrapolated to large volume conditions.

Buswell and Edwards[5] have shown that the unprecipitated aluminium in treated water is less than is ordinarily found in untreated natural waters even when the pH is far from the optimum. This should quiet the fears, expressed occasionally in medical circles, of the physiological effect of the "alum" used in water purification.

While the pH determination has not proved the panacea some would have led us to expect, it has already proved its usefulness in the operation of certain filter plants, notably the one at Baltimore.[6] The colloidal phase of the problem is generally recognized; yet, with the exception of the work of Catlett[7] and of O. M. Smith[8] and some theoretical proposals by Pirnie,[9] little progress has been made along that line.

While the role of oxygen in causing corrosion has long been recognized, several articles[10] have recently appeared describing various devices for preventing corrosion by means of "deoxidation." These are in general of two types: (1) Filtering the water over iron or other metal turnings to "deoxidize" it, or (2) boiling out the dissolved gases. In some cases a combination of the two is used. Tillmans and Heublein[11] and later Kolthoff[12] have shown that, as would be predicted from the mass law, the presence of $Ca(HCO_3)_2$ lessens the solvent action of H_2CO_3 on $CaCO_3$. The amount of $CaCO_3$ which a water will dissolve is a measure of the "aggressive" CO_2 which is a different numerical value from "free" CO_2.

Don's[13] recent investigation of the adsorption of ammonium salts in sand filters recalls the much earlier work of Chick[14] on the same subject but from the standpoint of sewage treatment. The cause of surface shrinkage in filters has been attributed to adsorption.[15]

A symposium on tastes and odors was held at the last convention[4] of the American Water Works Association. Chlorine may be noticeable if present in excess or it may produce organic compounds which cause a "chemical" or "iodoform" taste. British operators recommend "antichlors" for the former and $KMnO_4$ for the latter.

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* [illegible]

The most serious recent trouble due to tastes was that produced by *Synuria* in New York City[16] supply. This taste was removed by treating with an excess of Cl_2. Another case is recorded in which an attendant attempted to dislodge by force a specimen of *Mephitis mephitis* (vulgarly known as skunk) which had perched on the water intake.

The obvious disadvantage of waiting 24 to 48 hrs. for bacteriological results to tell whether or not chlorine treatment has been sufficient, has led to the immediate popularity of the chemical "excess chlorine" test of Enslow and Wolman,[17] which can be read within half an hour. The study of filter plant loading by Streeter[18] has thrown considerable light on what may be expected from various purification plants.

No radical changes have taken place in the field of matter softening since the introduction of zeolites 10 or 15 yrs. ago. Comparatively little has been published on the zeolite base exchange[19] reactions outside the patent literature, but it is now apparent that the power to exchange bases is possessed by a large number of "alumino silicate" compounds.

Indican[20] as an indicator of pollution has been suggested. Various modifications of the hardness tests[21] have recently been proposed. Several attempts to develop a delicate test for phenols[22] in water have met with questionable success, apparently because of the interference of natural coloring matter. Scheringa[23] has recently investigated the N_2 cycle in water, and Nichols[24] has made a new study of the significance of nitrates.

The A. P. H. A. standard methods of water and sewage analysis have been revised with the coöperation of a committee from this Society and are to be published in the near future. *Public Health Engineering Abstracts*, issued weekly by the Treasury Department Public Health Service, covers American and foreign literature. The American Water Works Association has recently included an abstract department in its journal. Additional articles[25] of importance are mentioned in the Bibliography, page 842.

Stream Pollution

Probably the most important advance in this field has been along the line of analytical methods. The older tests, oxygen consumed from $KMnO_4$ and solids lost on ignition, were admittedly empirical and since there was little uniformity of technic among different workers there was small basis for comparing their results. No less than five different methods for the oxygen consumed from $KMnO_4$ are given by various authoritative textbooks. The estimation of the degree of pollution from the forms of combined nitrogen has not been found feasible. The present method, originally described by the Royal Commission on Sewage Disposal,[26] measures the amount of dissolved oxygen required to satisfy or "stabilize" the organic matter in the sample. This is accomplished by diluting the sample with an amount of aerated distilled or tap water sufficient to contain an excess of dissolved oxygen and then titrating the residual oxygen after a period of incubation (1, 2, or 5 days) at constant temperature (usually 20° C.). From the titration and the length of incubation the "biochemical oxygen demand" is calculated, or the results may be expressed as "1-day demand," "2-day demand," or "5-day demand." When first proposed this method met with some opposition in this country owing to the frequency of erratic results, and the method was not included in the 1917 edition of Standard Methods of A. P. H. A. The method had much to recommend it, however, on account of its similarity to natural conditions and was adopted for stream pollution investigations by the U. S. Public Health Service. Largely through the efforts of this Service[27] the sources of most of the troubles have been found and a satisfactory technic worked out, which will appear in the new edition of Standard Methods.

The results of the extensive investigation of the Ohio River by the U. S. Public Health Service are to be published in the near future. The report will contain much information on methods of stream study and the course of the autopurification reactions. The same organization has been making a study of the Illinois River, in which opportunity has been afforded for checking and improving their investigational methods. We may expect considerable improvement in the "tools" of sanitary chemistry as well as voluminous data on the particular problems studied as the result of these investigations.

A symposium[28] on "Stream Pollution and Sewage Disposal" held at a meeting of the American Society of Civil Engineers in New York in November 1921, together with the discussion which followed, contains considerable information of a chemical nature. Donaldson[29] has reported on the relation of coal and oil, tannery, paper, and various other industrial wastes to water supplies. The limit of 200 to 400 p. p. m. of chlorides which has been set[29,30] on the allowable pollution from oil-well wastes and sea water seems to the writer to be unjustifiably low. Several cases of ground-water supplies containing 1000 p. p. m. or more of chlorides could be cited, and there is evidence that vegetation[31] and cattle will tolerate 2000 to 3000 parts. Gould[32] has discussed the oxygen requirement of New York harbor and the various sources from which this demand may be met. He concludes that surface aeration is the principal source of O, while Purdy in the discussion calls attention to the importance of microörganisms and aquatic plants. Streeter in discussing the same paper calls attention to the fact that turbulence must be depended upon for rapid aeration.

Sewage Purification

Activity in conserving nitrogen has been largely devoted to the development of the activated sludge process which is discussed in a separate article. Richards and Weekes[33] have proposed straw filters for sewage disposal and find that the bacterial growths which occur, fix ammoniacal and nitrate nitrogen. After a time the straw is replaced and, because of the nitrogen accumulated in the bacterial growths, the used straw is good for fertilizer.

Ardern[34] has discussed sewage disposal with reference to colloid chemistry, and he gives an excellent summary of the various theories of sewage purification together with valuable lists of references. He favors a middle ground between the biochemical and colloidal theories.

Cox[35] considers that the microbial growths on trickling filters are of greater importance than they are usually deemed to be. He gives lists of organisms found and concludes that the flora and fauna of the filter determine the biochemical reactions produced. Thompson[36] has made a similar study of trickling filter biology, more especially with reference to activity of enzymes which he proved were produced.

Wagenhals[37] concludes from an extensive engineering and chemical survey of sewage treatment plants that the Gooch crucible determination of suspended matter and the five-day biochemical oxygen demand at 20° are the best tests for determining the efficiency of sewage treatment plants. The paper contains considerable chemical data. Buswell and Weinhold[38] call attention to advantages of the ultra filter over the Gooch crucible, *viz.*, portability, speed, and the fact that it may be calibrated to give a notion of the size of colloidal particles. Mohlman and Pearse[39] have reviewed the various methods for estimating colloids and have suggested the use of the nephelometer.

No attempt has been made to cover the field of disinfection and industrial hygiene.

BIBLIOGRAPHY

1—[illegible], *J. Ind. Eng. Chem.*, **7** (1917), 289.

2—[illegible], *Chem. Met. Eng.*, **24** (1921), 728.

3—Buswell and Greenfield, *J. Am. Chem. Soc.*, **44** (1922), 1435.

4—[illegible], American Water Works Association Convention, May 18, 1922.

5—[illegible] and [illegible], *Chem. Met. Eng.*, **26** (1922), 826; Howard and Hannan, *Can. Eng.*, **41**, 461.

6—[illegible], *J.* [illegible], **9**, 408.

7—G. F. Catlett, *Eng. Rec.*, **73** (1916), 741.

8—O. M. Smith, *J. Am. Chem. Soc.*, **42** (1920), 460.

9—[illegible], *J. Am. Water Works Assoc.*, **9**, 247.

10—P. J. West, *J. Ind. Eng. Chem.*, **14** (1922), 601; F. N. Speller, *J. Frank. Inst.*, **193**, 515; P. J. Kestner, *J. Soc. Chem. Ind.*, **40** (1921), 57T.

11—J. Tillmans, *Z. Nahr.-Genussm.*, **38** (1919), 1.

12—J. M. Kolthoff, *Chem. Weekblad*, **17**, 390.

13—J. Don, *Engineering*, **111** (1921), 759.

14—Chick, *Proc. Roy. Soc.*, **57B**, 254.

15—Wolman and Powell, *Eng. News-Record*, **85**, 210; Gavett, *Ibid.*, 1081.

16—*Eng. News-Record*, **88**, 266.

17—Enslow and Wolman, *J. Ind. Eng. Chem.*, **11** (1919), 209.

18—H. W. Streeter, *J. Am. Water Works Assoc.*, **9** (1922), 157.

19—A. Gunther-Schultze, *Z. anorg. Chem.*, **116**, 16; *J. Soc. Chem. Ind.*, **40** (1921), 526A; Hisschemoller, *Rec. trav. chim.*, **40**, 394; *J. Soc. Chem. Ind.*, **40** [illegible] A.

20—Jolles, *Ber. pharm. Ges.*, **30** (1920), 421.

21—*C. A.*, **15** (1921), 1773, 910, 3354; **16** (1922), 2189.

22—Fox and Gauge, *J. Soc. Chem. Ind.*, **41** (1922), 173T.

23—L. Scheringa, *Pharm. Weekblad*, **57** (1920), 1481.

24—Nichols, *J. Ind. Eng. Chem.*, **12** (1920), 987; *Bur. Standards, Sci. Paper* **367**.

25—*Proc. Am. Soc. Civil Eng.*, **47**, 653; *Eng. News-Record*, **87**, 392, **444**; *Rep. of Comm. 13 of Am. Ry. Eng. Assoc.*, **23** (1921), 242; *J. Soc. Chem. Ind.*, **40** (1921), 159T; *Eng. News-Record*, **87**, 771; J. Collins, *J. Ind. Eng. Chem.*, **12** (1920), 1181; "A Half Century of Public Health." Edited by Ravenel. Jubilee Historical Volume of American Public Health Association.

26—8th Report of Royal Commission on Sewage Disposal, Appendix, 182.

27—E. J. Theriault and Hommon, *U. S. Pub. Health Bull.* **98**, 71; *U. S. Pub. Health Repts.* **35**, 1087.

28—*Proc. Am. Soc. Civil Eng.*, **47**, 617 (discussion in following number).

29—W. Donaldson, *Am. J. Pub. Health*, **11**, 193; **12**, 421.

30—*Eng. News-Record*, **86**, 513.

31—*C. A.*, **15** (1921), 3352.

32—Gould, *Proc. Am. Soc. Civil Eng.*, **47**, 603; **48**, 711, 991, 1269.

33—Richards and Weeks, Report from *Water and Water Eng.*, **23**, 500.

34—Ardern, "Second Report on Colloid Chemistry and Its General Industrial Applications," **1918**, 81.

35—Cox, *Eng. News-Record*, **87**, 720.

36—Thompson, *N. J. Agr. Expt. Sta., Bull.* **352** (1921).

37—Wagenhals, *U. S. Pub. Health Rept.* **37**, 1505.

38—Buswell and Weinhold, Paper, Philadelphia Convention, Am. Water Works Assoc., May 19, 1922.

39—Mohlman and Pearse, *J. Am. Water Works Assoc.*, **9**, 311.

40—Fairbrother and Benshaw, *J. Soc. Chem. Ind.*, **41** (1922), 134T.

41—*Pub. Health Repts.*, **37**, 275; J. S. Owens, *Proc. Roy. Soc.*, **101A**, 18 to 37; *J. Soc. Chem. Ind.*, **41** (1922), 344A.

Activated Sludge

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IT IS conceded that the activated sludge process is the most perfect method of sewage disposal at the present time. Its growth in America and European countries has been quite widespread. Since the discovery of the process, early in 1914, the method has been adopted for several municipalities, and an exceedingly large number of experimental plants have been put in operation. The most notable ones in existence at the present time are at Davyhulme (Lancashire), Worcester, Stamford, Aeritree, Sheffield, Bradford, Tunstall, Blackpole (Worcestershire), Whitney (Blanket Co.), St. Albans, Withington, Moreton (Dorsetshire), Birmingham, Reading, Baguely, and Stoke-on-Trent, in England. In other countries, the most notable ones are at Jamshedpur (India), Sibpur (India), Holte (Denmark), Burmeister (Denmark), and Kimberly (South Africa). In the United States the best-known plants are at Houston, Texas, and Milwaukee, Wis.

Edward Bartow

New Plants

Recently (April 1921) a plant has been installed at Woodstock, Ontario, to handle 1,500,000 imperial gal. per day, dry weather flow. A small plant has also been installed at Brampton, Ontario.

A plant was put in operation on October 18, 1921, at [illegible] N. [illegible] 1,000,000 gal. sewage daily.

In October 1921, an installation was put in operation to treat the waste (600,000-gal. daily flow) from the Decker Packing Plant at Mason City, Ia.

Experimental plants have been in operation for some time at Urbana, Ill., the Calumet region of the Sanitary District of Chicago; this plant when completed will have a capacity of 1,750,000 gal., and the plant of the Desplaines River district of the Sanitary District of Chicago, when completed, will treat the sewage from a population of 30,000.

In conjunction with the Corn Products Co., Argo, Ill., the Sanitary District of Chicago has also run an experimental plant on starch wastes. This plant has a capacity of 25,000 gal.

Experimental plants using mechanical agitation have been in operation at Pasadena and Hermosa Beach, Calif. Works are in the process of construction in Milwaukee which will treat the entire sewage from that city, population 588,750, and at Indianapolis, Ind., population 314,000. Other plants in the process of construction at the present time are Brisbane (Australia), and Singapore (India).

Rotheham, Hanley, and Mansfield (England) are considering schemes along the line of the Sheffield works. Los Angeles, Calif., is also considering the adoption of the activated sludge process for the treatment of sewage of that city.

There are many other small plants and installations that could be mentioned, but lack of space does not permit.

Types of Aeration

There are in general two types or modifications of aeration: (*a*) diffused air, and (*b*) mechanical agitation. The experimental plants in this country have practically all used the diffused air treatment, which consists of blowing air through the sewage and sludge, after it has passed through filtros plates.

Intermittent aeration has been tried at Manchester, England, and elsewhere; this allows aeration for a certain length of time and then a rest, but has not proved successful in the saving of air.

Certain devices have also been tried for decreasing the amount of air necessary for the process. The Dorr-Peck process consists in aerating the sewage and sludge in a specially designed thickener, which effects distribution and circulation of the air bubbles in one chamber and causes sedimentation in another. Aeration in less time and less air required was claimed, but the company very recently announced that the process had not met their expectations and they have decided to carry the tests no further. The Trent devices consist of aeration and agitation of the sewage by drawing the sewage and air into the bottom of the activation tanks. Distribution is by means of revolving perforated arms of the rotating lawn-sprinkling principle. Tests at Pasadena, Calif., and a similar process at Hermosa Beach, Calif., showed the process to take twice the time and cost more to operate than the continuous air diffusion method.

Mechanical agitation, that is, the use of revolving paddles, has proved successful at Sheffield, England. These paddles suck the air through a tube by creating a vacuum, and rotation is carried for eight hrs. By this method the sewage is brought in contact with the air at its surface only; the power required is to mix the sewage and induce a current, and by rippling the surface increases the surface exposed to the action of the air. The Sheffield sewage may be a special type, and experiments made elsewhere indicate that mechanical agitation alone will not purify sewage in the presence of activated sludge without the expenditure of much more energy than the air-diffusion method; the original and maintenance costs also seem greater.

It is the general opinion that the continuous air diffusion method is preferred but that some aeration might be dispensed with provided some other form is used.

Settling

Certain improvements over plain sedimentation are claimed for settling sludge. Dorr thickeners have been successfully used. These sedimentation tanks are circular in diameter and have a smooth bottom with a slight slope toward the center. A revolving scraper collects the sludge continuously, scraping it toward the center of the tank, from which it is removed by a pump or by gravity without the interruption of the operation of the thickener.

Dewatering Sludge and Sludge Drying

These are the biggest problems yet unsolved, but very promising advances have, however, been made within the last few months, and complete solution is hoped for in the near future. Filter pressing and certain types of centrifuges have given promising results under varying conditions. Lagooning has also been somewhat satisfactory, but in this method the fertilizing value of the sludge is lost. Certain recent developments have been made, both in England and in this country, in filter pressing. In England it has been found possible to reduce 98 to 99 per cent moisture sludge to 75 per cent by spreading it on paper-makers' gauze or very fine screen gauze and applying a slight vacuum to the under surface; the thin cake thus produced can be readily dried in the air. In this country experiments with certain types of American filters (Oliver and American) embodying the same principle have recently given very satisfactory results.

Dewatering by plate presses and squeeze presses (Worthington or Berringan) has given promising results with sludge that has been treated before filtration. At Milwaukee by adjusting the reaction to a certain hydrogen-ion concentration with sulfuric acid, and by adding chromium or aluminium sulfate, the rate of pressing has been greatly increased.

A solid bowl centrifuge (Besco-Ter-Meer) has given much more promising results than other centrifuges at Milwaukee. This centrifuge is continuous and automatic in operation, and is devoid of all screens. It builds up a cake against a solid stationary plate and unloads it automatically. It has been possible to reduce the moisture to 72 to 75 per cent. With this machine the water does not pass through the cake but out over the top; the effluent contains a rather high percentage of the lighter and finer solids. There are those who believe that a centrifuge will be so perfected that it will solve the dewatering problem.

Another recent advance in the dewatering treatment of sludge is the Maclachlan process, or modifications of it. In this process the sludge is treated with sulfur dioxide, generated by burning sulfur, and live steam. In the Maclachlan process at Houston, Tex., the sulfur dioxide and live steam are applied to the activated sludge for 25 min., raising its temperature from 80° to 135° F. The sludge floats to the top and can be readily filter-pressed, yielding a cake with as low as 74 per cent moisture; the treated sludge may be dried on filter beds. Jackson and Doman report that the filtered sludge dries readily on hard, impervious ground when applied in depths varying from 4 to 16 in. Dehydration cracks appear in all cases within 24 hrs. At the end of the first day the moisture is reported as 77.1 per cent, in 3 days 59.7 per cent, and in 3 wks. 26.4 per cent.

The present trend in dewatering sludge seems in the direction of conditioning the sludge rather than the improvement of mechanical devices. Besides drying the sludge on beds with disposal in the lagoons, direct heat driers have been used with more or less success for the drying of filter-press and centrifuge cake. Drying experiments have been carried out with both direct and indirect heat driers, and indications are that drying in either form is an expensive process. It is generally agreed, however, that after the first 20 per cent of the water is removed the sludge more readily parts from the remainder.

Fertilizing Value

Dried sludge has been proved by various investigators[1] to have an excellent fertilizing value. The nitrogen content of the sludge has been shown to be equal in fertilizing value to the nitrogen of ammonium sulfate or dried blood, when applied to grains and vegetables. These results have also been borne out at Rothamsted. The nitrogen content of the sludge varies from about 4 per cent to 7 per cent, depending upon the type of sewage treated. It has been shown at Manchester that 21 per cent of the nitrogen of the wet sludge is immediately available for plant food, while only 8.15 per cent of the nitrogen of airdried sludge and only 4.6 per cent of that dried at 100° C. are immediately available. Heat drying lowers the percentage of nitrates considerably.

One of the new developments is irrigation and fertilization with wet activated sludge. It is possible to dispose of the sludge already in liquid form by means of a system of mains and service pipes.

The present indications are that the sale of fertilizer will partially, if not wholly, offset the cost of the dewatering and drying of the sludge, if these problems are properly solved, but no surplus applicable to the operation of the plant can be expected.

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[1] Bartow and Hatfield, Nasmith, and others.

By-product Coking

By F. W. Sperr, Jr.

[illegible] The Koppers Company Laboratories, Mellon Institute, Pittsburgh, Pa.

THE BY-PRODUCT coke industry has found the past two years remarkably rich in technical achievements which promise a very prosperous development as business recovers from its recent depression. It is gratifying to note that such achievements are more and more the result of planned scientific research in which chemistry has a most important part. The field of research, comprising coal and its relation to coke formation, the coking process, the properties and utilization of coke, the recovery and utilization of the by-products, and the materials of plant construction, is so large, that a review of the subject condensed to the limits of this article would amount to a mere index of the numerous important papers that have appeared. It will, therefore, be more interesting and useful to select for discussion a few subjects of investigation that may be considered typical of the general trend of research in this connection.

F. W. Sperr, Jr.

Property and Process of Coking

The various investigators who have been working on the difficult and important problem of coal constitution have contributed much toward improving our conceptions of the coking property and the mechanism of coke formation. At the best, however, any such conceptions must be regarded as working hypotheses which we must be prepared to amend or to discard altogether in the light of additional information. Coal research is still in too early a stage to formulate strict generalizations, and investigators must not lose sight of the marked individuality possessed by each and every coal.[1]

The three general methods most used in recent investigations of coal constitution are examination with the microscope, solution in organic solvents, and low temperature distillation. It may be useful to attempt a brief correlation of the work so far done.

The study of coal with the microscope has been of prime importance with respect to the direct value of the results obtained. It has shown, what is now generally accepted, that an important group of coal constituents are resinic compounds derived from plant resins that are resistant to decay. These resinic compounds are believed to have a great influence on coke formation. Regarding the nature and influence of the other coal constituents our knowledge is most unsatisfactory. There was formally a disposition to classify these [illegible] pointed out that cellulose [illegible] of peat formation [illegible] action of pyridine on coal, and of the solubility of portions of the pyridine extract [illegible] the coal [illegible] the nature of each group. [illegible] working [illegible] definitions:

1—The alpha compounds are insoluble in pyridine.

2—The beta compounds are soluble in pyridine, but are left as insoluble residue when the pyridine extract is treated with chloroform.

3—The gamma compounds comprise that part of the pyridine extract which is soluble in chloroform.

The gamma compounds are considered to correspond with the resinic substances. As to the nature of the alpha and beta compounds we may refer here to the hypothesis of Fischer and Schrader[3] that lignin degradation products, rather than cellulosic substances, play an important part in coal constitution.

The relation of these three groups of substances to the coking property has been investigated by S. Roy Illingworth,[4] who worked with the general idea of determining the proportion of each group in the residues obtained by heating typical coals for different periods and at different temperatures. He found the beta compounds to be less stable than the resinic compounds and that in all probability the former are the first to decompose on heating. Assuming, as the majority of investigators have done, that the resinic compounds constitute the "cementing" agency in the coking process, he developed an interesting line of inquiry into the mechanism of coke formation on the basis of determining the minimum amount of these compounds that could be present to produce a coherent coke. His results indicated a difference in the cementing properties of the various resinic substances in the different coals—the higher volatile and more poorly coking coals having, as would be expected, resins with weaker coke-producing quality than the better coking coals. Nevertheless, he took 5.5 per cent of resinic substances to be an average figure for the majority of coking coals representing the minimum amount of resinic substances capable of holding a residue together in the form of a coherent coke. He then constructed a picture of the coking process showing the formation of a plastic stage due to softening of the resinic substances, the creation of a spongy state during the period when the mass contains more than the critical amount (*e. g.*, 5.5 per cent) of resins, and the stiffening and solidification of the mass with the reduction of the resinic content below 5.5 per cent. Differences in the porosity of coke he considered to be due to differences in the stability of the beta substances. The crucial characteristic of any coal as regards porosity of the resulting coke would be the amount of volatile matter evolved when the hot mass is in its most viscous state and about to pass to a fixed structure by virtue of the destruction of the resins. He determined the rate of evolution of volatile matter during what might be considered its critical period, and obtained "porosity factors" which came in the same order as the actual porosity of the cokes from the coals investigated.

Some space has been given to this work of Illingworth because it is typical of that type of scientific investigation which is greatly needed in coke technology. Work of this sort should be continued to the point of enabling us to determine definitely by a laboratory examination of any given coal the quality of the coke that it will make in large-scale operation, and this should be accomplished without the necessity of large-scale tests.

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[1] [illegible]

[2] [illegible] 1918

[3] *Brennstoff-Chem.*, **2** (1921), 37, 237.

[4] *J. Soc. Chem. Ind.*, **39** (1920), 111T, 133T; *Fuel*, **1** (1922), 49. See also Bone, *et al.*, *Proc. Roy. Soc.*, **100A** (1922), 582; reviewed and severely criticized by Wheeler in *Fuel*, **1** (1922), 49.

The microscopic examination of coal has developed certain new terms with which coke technologists must become acquainted. Reference must first be made to the pioneer work of Dr. Reinhardt Thiessen,[5] of the U. S. Bureau of Mines, who has developed a technic of making thin sections of coal through which light can be transmitted to such a point that ordinary bituminous coal can be most thoroughly examined. The bright bands prominent in bituminous coal, he finds, represent parts of definite components of the woody parts of plants—that is, parts once pieces of logs or stems, branches, twigs, and roots, but now much compressed. Such parts of the coal he calls *anthraxylon*, meaning coal wood, from *anthrax*, coal, and *xylon*, wood. Dr. Thiessen is now making a study of the relation between the constitution of coal, as seen under the microscope, and its coking quality, and has been making considerable progress in following this relation. For example, anthraxylous constituents of Illinois coal have been separated on the stage of the microscope and subsequently coked. The experiment showed that the anthraxylon swelled, fused, and acted as a coking constituent, whereas the attritus did not swell or fuse but merely sintered, retaining the original structure that it had in the coal.

This line of investigation has been pursued in England by Marie C. Stopes,[6] who distinguishes two constituents of the bright coal bands, *viz.*, *clarain* and *vitrain*. Clarain has a bright, smooth structure but is so closely associated with fragments of the dull coal (durain) as to be difficult to separate. Vitrain occurs in brilliant, structureless, well-defined bands. It can readily be separated and is usually smaller in amount than the other constituents. The other two principal constituents she calls *fusain* and *durain*. Fusain is the familiar "mother-of-coal" or "mineral charcoal." Durain is the dull-appearing coal substance (Mattkohle) having a hard, close, firm texture and a lumpy, irregular surface of breakage across the bedding plane.

Rudolph Lessing[7] has studied the behavior of these constituents on coking. Considerable fusion and merging of particles was shown by clarain which gave cokes with a peculiar brown sheen. Vitrain produces a characteristic silver-white coke, but the consolidation of particles did not go so far as with clarain. Durain was practically devoid of coking value, but the particles adhered to each other a little more than in the case of fusain which had absolutely no coking tendency.

A study of the properties and process of by-product coking is not complete without consideration of the light shed by low-temperature distillation, in which field there has been considerable activity directed toward the development of commercial processes. So far, however, the by-product chemist is chiefly concerned with the theories of pyrogenesis and coal structure, such as are developed in the recent articles of J. J. Morgan and R. P. Soule[8] on the composition of low-temperature tar, and their reference to earlier work of the same nature.

The very important problem of the deterioration of coal in storage has been studied by William Seymour,[9] both in relation to coke manufacture and to the utilization of the coke in the blast furnace.

A brief research of an entirely new type into the carbonization of coal has been conducted by Eric Sinkinson,[10] who has shown that the electrically nonconductor coal changes to a conductor (coke) at a temperature in the region of 500° C.

Reference should be made to the investigations of F. Korten[11] into the expansion of certain types of coal during coking. Our own laboratories have done a large amount of work on this subject, and have developed a method which, on a relatively small sample, determines both the coking qualities and the contraction or expansion of a given coal. This work will be published in the near future.

By-product Formation

So far, we have been considering that type of investigation which aims at the elucidation of the coking property. Other investigations into the phenomena of carbonization have to do with the evolution of by-products and during the past two years attention has been paid principally to ammonia and sulfur. Extensive experiments in full-sized by-product ovens have been described by A. Thau.[12] The characteristics of the coke, gas, light oil, etc., produced at different temperatures were examined but the principal work was done on the conditions covering the yield of ammonia. The amount of free space above the coal in the oven did not appear to have so much influence in decreasing the yield of ammonia by secondary decomposition as has been generally believed. The hot surfaces of carbon appear to be more effective in general secondary decompositions than the hot oven walls. Air leaks were shown to diminish the yield of ammonia considerably.

H. J. Hodsman[13] refers to the work of Thau and others, and describes laboratory experiments made under his direction to examine further the decomposition of ammonia in the presence of oxygen. No destruction of ammonia was detected in coal-gas mixtures containing 1 per cent of oxygen at any temperature below 600° C. At 700° C. and higher, the loss of ammonia was very considerable. The results of these experiments agreed in general with Thau's observations.

Another laboratory research into the formation of ammonia during carbonization was conducted by A. C. Monkhouse and J. W. Cobb.[14] Cokes prepared at 500°, 800°, and 1100° C. were subjected to the action of hydrogen and nitrogen separately at three different temperatures—600°, 800°, and 1000° C. The hydrogen appeared to exercise a specific action on the nitrogen in the 500° coke, with the formation of ammonia. Another series of experiments was made on the 500° coke treated successfully at 800° C. with nitrogen, hydrogen, and steam, the action of each gas being carried to completion before the next was allowed to act. Large quantities of ammonia were obtained by the use of hydrogen when heating with nitrogen had ceased to yield any ammonia, and further large quantities were obtained with steam when the hydrogen had become practically ineffective.

Monkhouse and Cobb also obtained some data on the liberation of sulfur from the coke under the above conditions. The sulfur was evolved as hydrogen sulfide in a way similar to and parallel with that of ammonia. A much more extensive investigation of the behavior of sulfur during carbonization has been conducted by Alfred R. Powell, of the U. S. Bureau of Mines. U. O. Hutton and C. C. Thomas,[15] of

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[5] *U. S. Bur. Mines, Bull.* **117** (1920), and other publications.

[6] *Proc. Roy. Soc.*, **90B** (1919), 470.

[7] *J. Chem. Soc.*, **117** (1920), 247.

[8] *Chem. Met. Eng.*, **26** (1922), 923, 977, 1025.

[9] *Blast Furnace and Steel Plant*, **1920**, 435.

[10] *J. Chem. Soc.*, **117** (1920), 839.

[11] *Stahl u. Eisen*, **40** (1920), 1105.

[12] *Brennstoff-Chem.*, **1** (1920), 52.

[13] *Gas World*, **76** (1922), 12 (Coking Section).

[14] *Gas J.*, **156** (1921), 234.

[15] This Journal, **12** (1920), 1077; **13** (1921), 33; *Gas Age*, **47** (1921), 88.

Johns Hopkins University, have also carried on a line of research in coöperation. Powell's work has been of great importance in showing the way in which different forms of [illegible] and the effect of hydrogen in removing [illegible] and has formed a basis for the study of methods for desulfurizing coke during the coking process which the Bureau of Mines is now conducting.

Properties and Utilization of Coke

In the work of our own laboratories in the Mellon Institute, great emphasis is placed on the study of coke itself. This has a twofold relation—first, to the conditions of coking, and second, to the conditions under which coke is consumed. A thorough knowledge of the properties of coke is essential. For some time especial attention has been given to specific gravity, porosity, and cell structure. The correct determination of the true specific gravity of coke is a problem, the difficulty of which is not generally recognized. The figures obtained vary with the method used, and since the porosity is calculated from the specific gravity, the discrepancies may be equivalent to as much as 30 to 50 per cent of the total variation in porosity found in different blast-furnace cokes. The subject has been fully discussed by H. J. Rose, of our laboratories, in a paper presented at the last meeting of the American Chemical Society. Methods of recording and comparing the cell structure of cokes have been developed, and much progress has been made toward a better understanding of this important characteristic.

Studies have also been made of the volatile matter and occluded gases in coke, in which connection the large amount of research work recently done by different investigators on the properties of charcoal has been found especially helpful. A study of the combustibility of coke is also under way. The investigation of the effect of the conditions of by-product coke oven operation on coke quality has led conversely to the development of a method that enables us to determine the maximum temperature to which a given piece of coke has been subjected.

Since 90 per cent of all coke manufactured is consumed in the blast furnace, the study of the effect of coke quality on blast-furnace operation is of prime importance. The most outstanding contribution to our knowledge of this subject has been made by Heinrich Koppers.[16] Extensive reference is made by Koppers to the work of H. P. Howland[17] on American blast-furnace practice. Koppers agrees with the general opinion of experts in this country that the most important property of coke for blast-furnace purposes is combustibility. He then shows the remarkable fuel consumption figures obtained in charcoal furnace practice and the significance of such practice with relation to the optimum coke quality. The combustibility of coke stands in close relation to the temperature of coking; the higher this temperature the less the combustibility. Good blast-furnace coke ought to be made of homogeneous coal coked at moderate temperatures in such a way that the heating is uniform at all points in the coking mass, and should be pushed out of the oven as soon a coking is finished. Finally, it should be uniform in size. Koppers shows how the by-product coke oven structure may be modified to attain a greater uniformity of heat flow into the coking mass. Great progress has been made in this direction in recent American installations, and the Becker type ovens, which have recently been put into operation by The Koppers Company at Chicago, may be cited as the newest development that has been made with remarkably successful results in the regulation of the quality of the coke produced.

Koppers goes much further than the regulation of coke oven conditions to produce the right sort of coke. He shows how the blast furnace itself may be improved by modifications, simple yet almost revolutionary in their conception, so as to obtain more uniform operation, increased capacity, and decreased coke consumption per ton of iron.

The relation between the physical properties of coke and its utilization in the blast furnace is being made a subject of study by the U. S. Bureau of Mines.

The various physical tests, such as shatter, hardness, porosity, and combustibility, are being thoroughly investigated at both the Southern Experiment Station of the Bureau, located at Tuscaloosa, Ala., and the Pittsburgh Experiment Station, as well as at the Experiment Station at Minneapolis, Minn. The rate of combustion of coke in various blast furnaces is being studied by taking samples of the hearth gases from a water-cooled sampling tube inserted in the tuyeres. By determining the relative percentages of carbon monoxide, carbon dioxide, and oxygen at various points in the hearth from the end of the tuyere to the center of the hearth, it is possible to note the variation in the rate of combustion in various blast furnaces using different kinds of coke. Laboratory experiments are also being made on the rate of combustion of coke of various physical properties.

Materials of Plant Construction

The most important materials in the construction of by-product coke plants are the refractories. Testimony before the Federal Trade Commission[18] shows that the by-product coke oven industry in this country stands second only to the open hearth industry in the consumption of firebrick. Modern American coking practice uses silica brick exclusively, which permits higher temperatures with consequent important decrease in coking time and increase in capacity. In this development, America is pioneer and the attention of the rest of the world is at present directed toward the adoption of this practice.

Advances in the production and utilization of other materials of plant construction have occurred during the past few years, but such advances have been shared in common with a great many other industries which also use these materials, so a detailed description is not in place here.

The Recovery of By-products and Other Developments

The preparation and utilization of the chief by-products, tar, ammonia, and benzol, each constitute an important industry in itself and the developments cannot adequately be considered in detail. In the tar industry, chief attention at present is given to the development of satisfactory processes for continuous distillation. The major attention of the ammonia industries has been directed toward the improvement of the chief product, ammonium sulfate, to give a neutral friable salt. This development is going forward mainly in England. The enormous war-time demands for benzol products have, of course, disappeared and research in this field has largely been confined to the development of a satisfactory motor fuel.

Other recent developments which give important economic aid to the advance of the by-product coke oven industry are the utilization of by-product coke oven gas as a domestic fuel, the firing of by-product ovens by producer gas (with the consequent release of a large amount of high-grade gas), and the liquid purification of gas.

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[16] [illegible] 1921 [illegible]

[17] [illegible] 56 [illegible]

[18] R. M. Howe, *Trans. Am. Inst. Min. Met. Eng.*, **62** (1919), 14.

The Anaconda Copper Mining Company has purchased a $1,000,000 phosphate rock deposit, intending to use waste smelter gases for fertilizer making.

Shale Oil

By Ralph H. McKee

Professor of Chemical Engineering, Columbia University, New York, N. Y.

THE DRAINING of natural resources is deplorable but the material gain resulting from their exploitation should not be overlooked. The approaching exhaustion of American petroleum has been compensated for in a large measure by the advances of American industries which this petroleum has made possible. Crude petroleum and "topped" petroleum are used as fuel in competition with coal. The present primary use of petroleum, however, is in the form of refined products, of which gasoline and lubricants are the most important. At present gasoline yields more than one-half the total revenues, though in volume it constitutes only one-fourth of the entire output.

Allman & Co.

Ralph H. McKee

The Gasoline Situation

The petroleum requirements of this country are closely bound up with the automobile industry. In 1900, when automobiles first became commercial, the yearly per capita consumption of petroleum in the United States was 35 gal.; in 1910 it had risen to 96 gal., in 1920 to 210 gal., and last year the increase, in spite of the financial depression, was still another 21 gal. per person. All this is in spite of a continual increase in gallons of gasoline obtained from each 100 gal. of crude oil. In 1915 each 100 gal. of crude oil gave 11 gal. of gasoline, but six years later the development of cracking had increased this to approximately 26 gal. If all the petroleum used in America were subjected to the cracking process, the amount obtained would be but about 40 gal. for each 100 gal. of crude petroleum.

In the last six years the gasoline used in the United States per automobile has decreased from 600 gal. per year to approximately 400 gal. per year, owing not to a decrease of mileage per car but to an increased efficiency of carburetors and engines. Were it not for this increased efficiency, we should already have reached our limit of gasoline consumption and with it probably a price of at least 40 cents a gallon.

Since 1921 the United States has been consuming more petroleum than it produces. This excess has been largely provided by Mexico and last year showed an importation of more than 120,000,000 bbls., that is, approximately 26 per cent of the American production. The Geological Survey and Bureau of Mines have lately shown that American production is approximately at its peak and that in a very few years the output of oil in the United States will begin to decline. Moreover, about a year ago the Geological Survey called attention to the fact that we should not expect to find any more large fields of petroleum in the United States—in other words, that practically all of the possibilities in the way of large petroleum fields in this country have been well prospected and that now we can calculate fairly closely what the production will be in the future.

On the other hand, the use of motor vehicles in this country is continually increasing. At present there are about 10,000,000 passenger cars, trucks, and tractors in use, and it is certain that the saturation point is more than 15,000,000 and perhaps will exceed 20,000,000 machines. With this expected larger demand for gasoline on one hand, and, on the other, even less petroleum available in a few years than we have at present, there arises a question as to how the motor fuel deficit is to be met. Of course, importations of oil can be made from Russia, Persia, Mesopotamia, and South America (the present Mexican fields are of short-lived type), but such an importation basis means that we shall be on the same basis as other importing countries have been, that is, the consumer will purchase his gasoline at from 60 to 75 cents a gallon. If our automobile industry and the many industries that depend on automobile transportation are to prosper, we must have a domestic supply of motor fuel and at a price more reasonable than 60 cents a gallon. Thirty-five or forty cents a gallon will probably be considered a fair price by the consumer.

Alcohol and benzene and the synthetic motor fuels having a mixture of these two as their base, will meet a small, but only a very small, portion of the needs. The total amount of these two motor fuels available in America is but a small percentage of the 20,000,000 gal. of gasoline now used daily.

Oil Shale Resources

In the last two years another source of motor fuel has begun to be considered seriously in America. In Europe oil shale has been used for nearly a century for the obtaining of petroleum. Indeed, the word "petroleum" was used for shale oil for a generation before Colonel Drake drilled the first oil well (Titusville, Pa., 1859). Oil shale does not contain petroleum, but by heating oil shale a petroleum distils from which a motor spirit similar to ordinary gasoline may be obtained.

The European oil shales yield 20 to 22 gal. of oil per ton of shale mined. In this country we have large deposits of shales that give double this yield of oil. The largest of these are the Green River deposits in Colorado, Utah, and Wyoming, but there are also deposits in Kentucky, Indiana, and Ohio, and some of equal extent in New Brunswick and Nova Scotia. Many of these will yield a barrel (42 gal.) of oil per ton of rock. For a typical oil shale view see Fig. 1. It is not commonly appreciated how large these oil shale deposits are. In the Green River section alone, there are known deposits yielding a barrel or more of petroleum per ton. These are sufficient to furnish more than five times the total world production since the commercial development of well petroleum 60 years ago.

Experimental Work

In the last two years "conversations" regarding shale oil possibilities have been followed by real experimental and small-plant operations, so that to-day we have several processes in course of trial. It is as yet a question whether we have found the best method of obtaining oil from the shale. It should be said in passing that the American shales do not work satisfactorily when retorted in the standard Scotch retort, and that, accordingly, modifications of this retort or retorts on new principles must be designed. So far the developments have been largely in the hands of mining engineers or of men without technical training. Only lately have chemical engineers taken an active hand in the industry.

It should be mentioned in this connection that perhaps the two most active nonfinancial organizations that have been working on shale oil are the United States Bureau of Mines and the Colorado School of Mines. The first has been criticized as being too conservative in its view in connection with this new industry; the second has been equally criticized for too optimistic a view.

[illegible]

Patents almost without number, most of which have their prototypes in the early Scotch industry, have lately issued from the Patent Office. A number of these have fallen into the hands of promotion companies and are now being made [illegible]. At present, few except the inventor himself believe that any of these retorts is certain [illegible] large scale.

[illegible] Co., Elko, Nevada, has apparently passed beyond the primary troubles in retorting, and has built a refinery to handle the crude shale oil and furnish the market with refined products. This plant has a capacity of approximately 15,000 gal. (350 bbls.) a day, a small capacity compared with commercial well petroleum plants.

About a year ago, it was shown that the organic matter in shale decomposes on heating, not to give petroleum directly but first to give a heavy solid or semisolid bitumen, and that petroleum is formed by a secondary cracking process from the first formed semisolid bitumen. This cracking process by which petroleum is formed is a liquid-phase process similar to the well-known phenomenon of the cracking of petroleum to give gasoline. Accordingly, it is not surprising that when shale oil is further cracked to give a motor spirit, the product carries 60 to 70 per cent of unsaturated hydrocarbons.

It was further found in the experimental work just referred to that decomposition of the organic material of the shale to give a semisolid bitumen occurred at a quite definite temperature (400° to 410° C.), and that the cracking process to obtain a petroleum from this took place approximately at but 20° higher.

The same investigation also showed to be incorrect the common belief that on heating, gasoline is the first product; on higher heating, kerosene; and on still higher heating, lubricating oils, etc. In other words, all these products are formed simultaneously by the cracking of the semisolid bitumen first formed.

It has not yet been possible to obtain heavy type lubricants, such as a cylinder oil, from shale oil. On the other hand, recent work has shown that excellent lubricants of light body can be made. It is worth mentioning that these lubricants, unlike ordinary well petroleum lubricants, do not decrease in viscosity rapidly on heating and, accordingly, in light use, such as in an automobile, the mileage obtained has been unexpectedly great.

Considerable gas is produced in the making of shale oil. Under the best conditions the amount of this gas is not sufficient for the fuel required in the retorting process. In Scotland they have supplemented the gas by using local coal for the shale retorts. With the American shales, which are richer in organic material than the Scotch, there is enough carbonaceous residue left (20 per cent) in the shale to permit it to be burned in a gas producer; in fact, one American plant is now regularly using this shale residue in a producer to furnish producer gas for the retorting of the shale. Most engineers would state offhand that a fuel running more than 75 per cent ash would not burn in a producer, but it does.

BY-PRODUCTS

In the French and Scotch shale-oil plants the production of ammonia in the process is as important as the production of oil. The American shales give less ammonia, but still enough to make it worth while to recover it. If the shale is retorted at only moderate temperatures, as most American shales will be, there is obtained a large percentage (up to 20 per cent) of nitrogenous constituents in the oil. These nitrogenous constituents are largely pyridine and isoquinoline derivatives. Up to the present time, no commercial outlet for these products has been worked out. They will, no doubt, compete in the future with the nitrogen bases obtained directly or indirectly from coal tar.

Some of the western oil shales give considerable quantities of paraffin, a few as high as 30 per cent of the weight of the oil. The eastern and some of the larger western deposits have an asphaltic base and give little or no paraffin.

Irresponsible promoters have claimed that the residue from oil shale retorting carries considerable amounts of platinum, gold, and other precious metals, phosphates, and soluble potash. These claims have no basis of fact, except possibly a small percentage of potash which has been rendered soluble by the retorting process.

The demands for petroleum are increasing in this country at the rate of about 50,000,000 bbls. a year. We have in prospect no source of fuel oil, gasoline, or gasoline substitute other than oil shale that promises to furnish even a minor part of this demand. To meet this, even without making any allowances for the expected decrease in production from oil wells, will require each year the building of 75 shale-oil plants, each handling 2000 tons of oil shale daily, and each representing an investment of nearly a million dollars. And yet some men feel that the industrial need for chemical engineers and chemists is limited!

The Application of Chemistry to the Conservation of Motor Fuels

By **Thomas Midgley, Jr., and T. A. Boyd**

Chief and Assistant Chief, Fuel Section, General Motors Research Corporation, Dayton, Ohio

THIRTY years ago the first automobile had not yet been built in this country. To-day there are about 11,000,000 motor vehicles in the United States—one for every 10 persons in the country. In the early days of the automobile it appeared to be only a troublesome and very expensive luxury. But the phenomenal increase in its use, the most of which has occurred within the last ten years, indicates that the automobile is not a luxury but a necessity. It is a necessity because it meets in an admirable way one of the most fundamental needs of civilization, that of transportation. It has been said that the automobile represents the first great advance in individual transportation since man began to use the horse.

Thomas Midgley, Jr.

Need for Liquid Fuel

Automotive transportation, of which such a wide and essential use is now being made, and of which a large future expansion is assured, is dependent for its existence upon an adequate supply of liquid fuel. The use of motor vehicles has been built up around gasoline, a material which only a few years ago was a troublesome by-product of petroleum refineries. As the number of automobiles in use increased, this product, for which there had previously been very little demand, was gradually absorbed, until about 1905 there was no longer a sufficient supply of the early highly volatile gasoline to operate the motor vehicles in use.

At this point gasoline began to assume a higher place in refinery economics. It was no longer a by-product; but its production was extended in order to keep pace with the development of motor transportation, until it has now assumed prodigious proportions. In 1921 the production of gasoline in the United States was over 5,000,000,000 gal.[1] This means that the petroleum refineries in the United States are filling a 10,000-gal. tank car with gasoline every minute of the year.

Since 1909 the number of motor vehicles in use in the United States has increased over 3000 per cent, while during the same period the production of petroleum has increased only about 150 per cent. The amount of gasoline necessary to keep this rapidly increasing number of motor vehicles in operation was supplied by refineries from a production of petroleum that did not keep pace with the rising demand for motor fuel: (1) By putting an increasing percentage of the distillate from the crude oil into the gasoline fraction; (2) by cracking heavier oils; and (3) by extracting liquid hydrocarbons from natural gas.

With the possible exception of further increases resulting from the cracking of heavier oils, the limit of the percentage of gasoline that can be obtained from crude oil has almost been reached. In view of the situation that the production of petroleum has not kept, and apparently cannot keep, pace with the rapid increase in automotive transportation, this is a significant fact.

Future Supply of Motor Fuel

One of the most serious questions with regard to the future of motor transportation is that of the supply of liquid fuel. A number of producers of petroleum have expressed the belief that our reserve of petroleum will last indefinitely, and that there is every likelihood that no shortage of oil will occur.[2] In every case of this optimism that has come to our attention, however, no reason has been given for the opinion that our supply of petroleum is adequate for future needs.

A recent estimate of the petroleum reserves of the United States has been made jointly by the American Association of Petroleum Geologists and the United States Geological Survey. Their report, which was made public in January 1922, indicates that at the present rate of consumption the domestic reserves of petroleum are sufficient to meet the requirements of the United States for only about 20 yrs. Of the 15,000,000,000 bbls. of petroleum which, on the basis of this estimate, was in the ground originally, about 40 per cent has so far been mined; and over 450,000,000 bbls., or 5 per cent of the unmined reserve, are now being produced per year.

While this estimate of the geologists is necessarily based upon incomplete data and probably lacks the desired degree of accuracy, it is certain that our supply of petroleum is being rapidly depleted. If the domestic reserve of petroleum should be three times the amount of this estimate, it would last, at the present rate of consumption, only 60 yrs. It has been 60 yrs. since the Civil War. In view of this condition all possible conservation of materials that are suitable for motor fuels should be a matter of vital concern to every citizen.

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[1] The statistics used herein have been taken from the following sources: "Gasoline," Refinery Statistics of U. S. Bureau of Mines; "Petroleum and Coal," U. S. Geological Survey; "Automobiles," *Automotive Industries*, **46** (1922), No. 7.

[2] American Petroleum Institute, *Bull.* **132** (1920); **200** (1921).

Sources of Liquid Fuels, Other than Petroleum

There are three potential sources, in addition to petroleum, to which we may look for some part of our future domestic supplies of motor fuel:

> 1. Oils from Shale—The enormous deposits of shale in this country will undoubtedly be developed. But, even at the best, it will be many years before quantity production of motor fuel from shale can be obtained.
> 2. Oils from Coal—The light oils produced in the carbonization of coal make a desirable motor fuel. But, if all the bituminous coal mined in the United States in 1921 had been so treated as to yield 3 gal. of motor fuel per ton, the product would have amounted to less than 25 per cent of the gasoline produced during the same period.
> 3. Alcohol—Vegetation offers a source of tremendous quantities of liquid fuel, the utilization of which awaits only a proper cheapening and simplification of the process of converting cellulose to a liquid suitable for motor fuel.

The present production of liquid fuels from the three potential sources enumerated above is so small that, when compared with the enormous volume of motor fuel required, it is almost negligible. Therefore, while they offer a comforting reserve for the future, it will be many years before sufficient material can be obtained from these sources to supply any considerable percentage of the motor fuel requirements of the country. Some means must be provided to bridge the threatened gap between petroleum and the commercial production of large quantities of liquid fuels from other sources.

Increasing the Fuel Economy of Automotive Engines

The best way to accomplish this result is to increase the efficiency with which the energy of gasoline is utilized in automotive equipment, and thereby to obtain more "automobile-miles" per gallon of fuel. In itself, this is apparently a simple problem for the mechanical engineer to solve. It has been demonstrated repeatedly that large increases in fuel economy, or in number of miles per gallon of fuel, can be obtained merely by changing the gear ratio in the rear axle, so that the rear wheels make a greater number of revolutions per revolution of the motor than they did before.

But unfortunately this simple expedient is not a practical solution of the problem, because such a change in gearing produces a car that is lacking in accelerating and hill climbing ability to such an extent that people will not buy it. At the present price of motor fuel, economy is secondary to performance in the estimation of the public. Such a change in the rear axle gear ratio not only transforms the car, but it also converts what was a problem of mechanical engineering to an unsolvable one of salesmanship.

Nevertheless, this change is the correct first step toward better fuel economy. So the problem must again be referred to the engineer—not to the mechanical engineer, for he has done his part; but to the heat power engineer and the physicist. It is their problem to increase the torque delivered by the engine so that the car with the reduced gear ratio may regain its accelerating and hill climbing ability, and thereby become a product that the salesman can sell.

The solution of the problem again appears very simple. According to the laws of thermodynamics, both the torque and the fuel economy of an engine are increased as its expansion ratio (in automotive practice, called compression ratio) is raised. Logically, then, the next step is to increase the expansion ratio of the motor. This is accomplished by reducing the clearance volume above the piston, which in turn increases the pressure at which the fuel mixture undergoes combustion.

These changes, *viz.*, increasing the gear ratio at the rear axle, and increasing the expansion ratio of the engine, should theoretically produce an excellent automobile, one giving such high fuel economy that the salesman should have no trouble in marketing it. But the salesman's problem is still unsolved.

The "Knock"

This super-product of the mechanical and heat power engineers does not function properly; but, when running on gasoline, it gives a very objectionable and disturbing noise. This noise, which is metallic in sound, is called by motor mechanics a "knock," the term usually being qualified by an adjective such as "carbon," "spark," "heat" or "fuel." The knock, as it occurs in the automobile engine of the present, when it is laboring at wide open throttle, is familiar to everyone who has driven an automobile. But the degree of intensity of this knock increases with the pressure at which the fuel mixture is burned. So that, while in present-day automobiles the knock is so slight as to be merely an unpleasantness that does no harm, its intensity in this redesigned engine of considerably reduced clearance volume becomes so great as to result not only in loss of power but also in actual damage to the engine, such as cracked spark plug porcelains and broken piston tops. Because this phenomenon of the knock stands as an apparently effective barrier in the way of obtaining better fuel economies from automotive engines, its remedy is the key to the solution of a great economic problem.

The fact has been noted previously that this disturbance is frequently called a "fuel knock." This has arisen because its intensity is primarily a function of the chemical structure of the fuel used. Thus, the disturbance that is present in an engine when the fuel has the paraffin structure (gasoline) entirely disappears if benzene or alcohol is used. But the chemical structure of motor fuel from a commercial standpoint is at present fixed within fairly narrow limits. The use of petroleum oils as our commercial motor fuel is necessary on account of the enormous volume required, and because of the small amounts of other fuels available. Gasoline is an excellent fuel, except for the limitation it imposes upon economy on account of its tendency to knock. The final step in the solution of the problem, then, is to eliminate the knocking or detonating tendency of gasoline.

Elimination of the Knock

It is well known that if substantial percentages of benzene or alcohol are mixed with gasoline, the product can be used in motors of fairly high compressions without the objectionable knock. But unfortunately 40 to 60 per cent of one of these materials must be added to gasoline to accomplish the desired result; and so the amounts of benzene and alcohol available are sufficient to treat only a very small part of the gasoline that is consumed.

As the result of a large amount of work that has been done on this problem, a number of chemical compounds have been discovered which exert such an influence on the combustion of highly compressed mixtures of gasoline and air that in the presence of a small fraction of one per cent of one of these materials gasoline can be used as fuel in engines of very high compressions. Because of their remarkable effects, these compounds have been named "compressionizers" or "antiknock materials." Their effect is to change the combustion of highly compressed mixtures of gasoline and air in such a way that no knock results, but the burn becomes entirely free from the disturbances that characterize detonating combustion. Some of these compounds are over 500 times as effective as benzene. Thus, 0.04 per cent by volume of one of these materials in kerosene is equal in effect for the suppression of detonation to about 25 per cent by volume of benzene in the same kerosene.

A considerable number of these compounds of widely variant chemical compositions have been discovered. The results obtained in their investigation will be dealt with in a paper entitled "The Chemical Control of Gaseous Detonation with Particular Reference to the Internal-Combustion Engine," to be given at the September meeting of the American Chemical Society in Pittsburgh.

The addition of an antiknock material to gasoline makes it possible to obtain very much greater fuel economies, because it permits such changes in design to be made that the fuel can be used more efficiently. But, unless the intensity of the knock in a given engine is so great as to cut down power, the presence of an antiknock material in the fuel does not result in an increased fuel economy. Since the addition of a small percentage of such a compound makes very little or no change in the energy of a given volume of gasoline, no increase in the mileage obtained per gallon can result from its use, unless such changes are made in the engine that a larger percentage of the energy content of the gasoline can be utilized.

Some of these antiknock materials have been rather widely used, particularly in airplane engines, and their great effectiveness and value have been demonstrated thereby. In view of the remarkable effects of these compounds and the good results that have been obtained in their use, it seems certain that it will be only a matter of time until all gasoline will be treated with an antiknock material, and automobile engines having higher compressions and giving considerably greater mileages per gallon will be used. The principal effect of the use of antiknock compounds will be the much further removal of the time when the threatened exhaustion of our petroleum reserves will actually occur.

Scientific Method in Rubber Compounding

By C. O. North

The Rubber Service Laboratories Co., Inc., Akron, Ohio

VERY satisfactory progress has been made during the past few years in applying scientific methods to the problems of rubber compounding. This has been made possible through the development of new and improved methods of rubber testing which in turn have furnished us with a clearer conception of the underlying principles of compounding.

The first chemists to make a study of the art of compounding had before them the picture of steel. They were of the opinion that the problems of rubber could be solved in a similar manner and consequently laid great stress on the development and application of chemical analysis. For example, they thought that coefficient of vulcanization was by far the best index of state of cure. They failed to realize that in rubber we have a mingling of both chemistry and physics. While strictly chemical problems are met in the vulcanizing reactions, yet the effects of pigments and other compounding ingredients belong within the field of physics. The coefficient of vulcanization is merely a measure of the quantity of sulfur which has become added to rubber. It is in no way a measure of the state of technical cure because of the factor known as depolymerization.

Effects of Temperature and Type of Accelerator

It is now generally understood that in vulcanizing or curing we have two effects which work in opposite directions. Depolymerization or the reduction in size of the colloidal aggregates of rubber is a factor which tends to weaken or deteriorate the final product. It is influenced primarily by heat and the time of heating. For example, it is not a factor at cures made at 10 and 20 lbs. of steam pressure (namely, 239.4° and 258.8° F., respectively). This statement applies even when the time of heating is as long as from 3 to 5 hrs. As the temperature rises, the time within which depolymerization is not a decided factor grows smaller and smaller. At 40 lbs.' steam (287° F.) the range is from 1 hr. to 1 hr. 30 min. At 60 lbs. (307° F.) it has narrowed down to from 15 to 30 min. The higher the temperature, the shorter becomes the time within which rubber may be heated without serious deterioration.

Another factor which affects depolymerization is the type of accelerator employed. For example, *p*-nitrosodimethylaniline is a violent depolymerizer, as are several softeners or fluxing materials which are sometimes added to a compound for the purpose of making it easier to handle in the factory. Some softeners are powerful depolymerizers, others have little effect. For example, paraffin is quite pronounced in its action, but castor oil is quite inert.

Opposed to the depolymerizing action of heat and certain substances, we have vulcanization which ordinarily means sulfur addition. While we know many ways of reducing the size of the colloidal aggregates of rubber, yet we are limited to sulfur and sulfur chloride for commercial methods of linking them into larger units. Since vulcanization by sulfur chloride has such a small number of applications, it may be practically disregarded. Sulfur then is the principal depolymerizer. It counteracts the effects of heating and other depolymerizing influences. As will be readily appreciated, the more sulfur which must combine with rubber to produce technical cure, the poorer the product. For example, reclaims whose poor quality are well known will seldom be found to have a coefficient of vulcanization under 5. In other words, the combined sulfur will be more than 5 per cent of the rubber present.

On the other hand, Whitby's compounds vulcanized with various dithiocarbamates and cured in from 3 to 5 min. at 287° F. (40 lbs. steam) showed remarkably high tensile strengths with a coefficient of vulcanization seldom over 1.5 and ordinarily less than 1. It is therefore generally realized that the larger the colloidal aggregates in rubber vulcanized to the point of commercial cure, the greater the tensile strength, the resistance to tearing and flexing, and the more pliable and stretchy the article. Certainly when properly vulcanized such compounds have longer life and stand up better in service.

Aside from the advantage and more rapid turning over of equipment, shorter cures at moderate temperatures are very desirable because of the increased service and durability of the product so prepared. It will be remembered that a few years ago 3000 mi. was considered a remarkable record for pneumatic tires. In those days the cures were from 3 to 5 hrs. long. To-day a record of 10,000 mi. is considered only average. The curing time has been shortened from 3 hrs. to approximately 1 hr. for the small sizes. The large sizes have been reduced in proportion.

While there are other factors which have had a bearing on this problem, the fact remains that rubber cured with the aid of organic accelerators has a lower coefficient of vulcanization than formerly and a higher degree of polymerization than was ever met with in the old days.

Regardless of the advantage of shorter cures, the compounder is limited by the slow heat flow in stocks and fabricated articles. The heat conductivities of both rubber and fabric are low and therefore a very thorough understanding of the temperature effects must be had before one can secure a uniform cure throughout an article. This requires extensive thermocouple measurements and considerable mathematics in working out the generalizations. Fortunately work on this subject is now going forward in the laboratories of several companies and it is hoped within a short time to be able to calculate the temperature at any point within the tire or other article at any time under definite temperature conditions.

Assuming that one has a very thorough knowledge of the temperature conditions, we have then the problem of securing uniform cure throughout the article. For a long time we had to place entire dependence on what is known as a rising or step-up cure. When properly worked out this method does give practically uniform effects but with the introduction of the so-called flat curing accelerators these problems have been solved much more easily. By flat curing accelerators we mean those which are capable of giving uniform physical properties over a long range of time.

An accelerator is known which has a range of from 30 min. to 4 hrs. cure at 40 lbs. or 287° F. Within this range of cures all samples of this stock have shown perfect aging to date. This is really remarkable and certainly helps to smooth off any inequalities left by an improperly gaged rising cure.

PRACTICAL PROCEDURE IN COMPOUNDING

As in other industries the application of the scientific method usually follows the rule-of-thumb experiments carried on by the first investigators. When a compounder has the task of working out compounds and structural features which enter into the construction of an article, as for example a pneumatic tire, he must first familiarize himself with the behavior of articles which have given a good account of themselves in actual service. Thus, if he is working with tires, he will study various makes, determine the average life under different conditions, the rate of tread wear and deflection under which they have been run, the type of roads, and other conditions of service. He will select those tires which have given good service, or, as is usually the case, he will pick out one tire having the most satisfactory tread, another with the better bead or another with a better carcass, and in fact will make a study of the weak points of the articles then in service.

If it is steam hose he will determine the average life both by steaming tests and actual service. His first problem is unquestionably that of service rendered and the manner in which articles of other manufacture have met this service. With the above information he will then make a more careful [illegible] of the conditions of service and will determine, [illegible] extent of flexing, the maximum tensile strains which have been met, the conditions of wear, [illegible] escape, whether the service is continuous or intermittent, and he will make a special investigation of all conditions which are somewhat out of the ordinary.

He will then tear down those articles which have given the best service and make a careful analysis of them, basing his decisions both on tests after service has been completed and on the freshly manufactured article. For example, he will determine the tensile strength and ultimate elongation of the different compounds which enter into the article with as much accuracy as is possible. He will determine the stress-strain curves of the different stocks and will make particular note of the load required to produce 300 per cent elongation, which figure many compounders have now come to regard as the best index of stiffness. He will study the characteristics of the hysteresis loop and particularly the ratios of energy input and output at low elongations. Moreover, he will make careful note of the resistance to tearing, to abrasion, and to flexing. These three are perhaps the most important of all, and he will measure these resistances by tests which have recently been developed but which have not yet been standardized. He will determine the rate of plastic flow and of recovery. The union of the different parts of the article to one another will also be very carefully studied. This matter is of maximum importance, particularly in pneumatic and solid tires. Many tires fail through unsatisfactory unions between the plies or between tread and breaker, or between breaker and carcass. In solids a great deal of trouble results from separation between tread and hard rubber. In fact, this is the most serious type of failure and has caused the solid tire companies much concern.

Before going any further into the development of an article to meet any definite set of conditions, the compounder must make a careful study of the conditions of manufacture. Too often are we given to the bad habit of determining what we should have without regard to what we can make. The operations through which different compounds must pass in going from the unmanufactured to the finished state must be carefully worked out. The milling, calendering, and tubing conditions must be thoroughly understood, the curing conditions must be set and the rate of heat flow measured or approximated in order to determine the minimum time and the proper temperature of the cure. Moreover, a compound cannot be considered by itself but always in relation to other stocks and the union which it must make to them. In addition to this, the compounder is limited by competition to a certain definite cost for each stock and if possible he must reduce costs, at the same time delivering a product of equal or better quality. Again, appearance is usually a very large factor. He must make a special effort to produce an article pleasing to the eye.

It will be gathered from the above that the conditions which the compounder must meet in order to develop a satisfactory article are not only numerous but difficult to handle. Much of the lack of progress along scientific lines in the past was due largely to the multiplicity of factors which had to be considered.

In compounding to meet the fine conditions of cure, a knowledge of the behavior of accelerators is required, which as yet is little appreciated. Not only must one have at hand a great mass of data obtained at normal curing temperatures, but the behavior of the various accelerators with different sulfur and accelerator ratios to rubber in the presence of various activators, such as zinc oxide, lime, etc., must be known for various temperatures. As a rule it is perfectly satisfactory to work with the temperatures of 50, 40, 30, 20, and 10 lbs. of steam. Certain accelerators will not function below 30 lbs. of steam and there is at least one which is said not to function under 50 lbs. of steam.

After working out the effects of various accelerators and sulfur ratios in simple mixes, it becomes imperative to know the influence of various rubber fillers, oils, greases, and substitutes on such compounds. The principal difference will be found in the fact that oils, etc., require slightly higher sulfur ratios. With this information as a basis, it is possible to work out compounds which will cure within the desired range or time, and the average compounder will make a special effort to have this range as wide as possible. Certainly there are few purposes for which at least a 2-hr. range cannot be obtained; in other words, a compound which will give equivalent physical properties within a range of 2 hrs. For example, it should be possible for a stock which has certain definite characteristics at 1 hr. to be cured to 3 hrs. without serious change in physical properties. This does not mean of course that one should cure at 3 hrs., but in practically all cases we are much safer in the aging properties of the compound, if, having this range, we then cure to the optimum cure or slightly beyond it.

The next step is arriving at the proper plasticity in the raw stock. This plasticity enters into every phase of the fabrication of the article. For example, a tire friction must be soft enough to run directly on cord fabric without spreading the cords. It must thoroughly penetrate the cords and it must maintain a certain tackiness all the way through to the tire building operations, and at the same time it must not be so sticky as to stick to the liner or to work out badly on the bias cutters. This plasticity is also of importance in making a proper contact with other stocks, which is the first requisite in securing good unions. It also enters into the readiness with which stocks may be run on the calender and tube machines. This requires a very thorough study of softeners and their effects.

INFLUENCE OF FILLERS

From a study of articles and their constituent elements, one can usually arrive at the approximate physical characteristics of the compounds employed. Outside of cure and plasticity, the development of a compound for a certain purpose requires a thorough knowledge of fillers, which may be divided into the active and inert types.

This is hardly the place to go into the reasons for activity or inertness in a pigment but briefly it is now generally understood that activity is very closely tied up with fineness of division and the condition of particle surface. For example, micronex carbon black, which is by far the finest product commercially available at present, has a fineness of division of less than 0.1μ. Moreover, it is reasonable to suppose that its surface is not merely that of a spherical particle but probably is something of the nature of a feather. Regardless of the reason, carbon black continues to be our most important filler and the one which has the greatest toughening effect upon rubber. Within the last few months, however, certain new types of zinc oxide have been brought out which are much finer and carry lower impurities than the older grades and therefore are more reactive and show greater activation effects on accelerators and give higher tensiles and better stiffening action. To date there are no competitors of carbon black and zinc oxide. Clay has been advanced and has been found of value when used in small quantities. While it does have some of the desired stiffening action, yet because of the fact that there are many agglomerates and large particles present which do not disperse well in rubber, it has as yet only limited application in high-grade compounds. Not only must one pay special attention to the fineness of division and surface effects of fillers, but the degree of ease with which these fillers can be dispersed in rubber must be well understood. Dispersion experience in paint, glycerol, water, and other media does not necessarily hold and has little bearing on the ease with which a pigment may be dispersed in rubber. Methods of milling and the softeners employed have a great bearing on the subject and there is hardly a compounder who cannot improve his compounds by improving his milling characteristics.

Of the inert fillers none are very finely divided and consequently they cannot be dispersed very thoroughly in rubber. To this class belong certain grades of whiting, clay, barytes, and others which are used chiefly because they are cheap. In high-grade stocks where severe conditions of service must be met, it is unusual to find them present in any high percentage.

In reference to the rubbers which find the widest application at present it may be stated that one of the outstanding features of our present compounding is the wide use of brown crepe. This rubber mills nicely and furnishes desirable plasticizing properties to the resultant compounds. It is true that it does vary in rate of cure but in the presence of organic accelerators this variation is so masked that it is of little importance. A much more important problem is its variation in plasticity. Many companies are now making plasticity tests by milling a definite weight of rubber under carefully controlled conditions and determining the time required for breaking down to a desired degree.

There was a time when compounding and design were widely separated and there was very little coöperation between the two ends of the business. Fortunately, to-day the designer has taken up compounding or the compounder has taken up design. It has now become a recognized fact that the success or failure of any rubber article depends not only on the stocks employed and the technic of factory production, but also upon how well the mechanics of the articles have been worked out in perfecting the design. For years we have been putting too much fabric in our tires. This year has seen a decrease in the number of plies and we are soon to decrease the number of cords per inch in the plies. Sea Island and Egyptian cotton were formerly employed exclusively. To-day much karded and combed peeler will be found in many of the best tires.

CONCLUSION

In outlining the above, the writer has made no effort to go into detail on any of the big problems of compounding. His whole aim has been to point out the conditions which confront the compounder and the vast amount of information which he must have at hand in order to successfully meet the conditions of service and competition. It is hoped that this paper will serve as an illustration of the application of the scientific method to one of the most difficult branches of applied engineering.

Meeting of the American Electrochemical Society

The Forty-second General Meeting of the American Electrochemical Society will be held at Montreal, Quebec, and will be opened by President Schluederberg on Thursday morning, September 21.

The recently organized Division on Electrodeposition will be well represented. One of the papers of the Thursday morning session will deal with the physical properties of electrolytic iron—a product which is being prepared commercially, contrary to all predictions of ten years ago. There will also be papers on zinc, brass, and other electrodeposited metals.

The Thursday afternoon and Friday morning sessions of the Electrothermic Division will be given over to a symposium on "Industrial Heating," which will include the following papers:

History of Industrial Heating; Principles of Design of Furnaces; Comparison of Fuel Costs in Different Types of Electric Furnaces, and with Combustion Furnaces; Resistor Materials; Specific Heats; Electric Conductivity of Insulating Materials at Industrial Furnace Temperatures; Heat Emissivity; Heat Transfer.

A popular lecture on the Progress in Physical Science is scheduled for Thursday evening. Section Q will be in charge of an old-fashioned Smoker on Friday evening. A special train will be furnished for an all-day trip to Shawinigan Falls. Hotel Windsor will be headquarters for this meeting.

Physics of Rubber, 1920-1921

By W. B. Wiegand

MANAGING DIRECTOR, AMES HOLDEN MCCREADY, LTD., MONTREAL, CANADA

PERHAPS the most valuable publication of the period is "Plantation Rubber and the Testing of Rubber," by G. S. Whitby; Part II of which includes a review of the work on rubber by some of the master physicists of the nineteenth century. Nothing could be more fruitful than the repetition of much of this work, with with due regard to composition and life history of the mixings employed.

W. B. WIEGAND

PHYSICAL STRUCTURE

UNSTRAINED—The spatial distribution of discrete ingredients in vulcanized rubber has been admirably studied by Mr. H. Green,[1,*] whose photomicrographs show clearly the phenomena of dispersion and agglomeration. The extension of his work to uncompounded rubber may add to our knowledge of its ultimate colloidal structure and so supply visual confirmation or otherwise of the net work hypothesis of C. O. North,[2] and of the spheroidal theory of R. W. Lunn.[3]

STRAINED—The development of vacuoles at the poles of particles in strained rubber, predicted on theoretical grounds by H. F. Schippel,[4] has been visually confirmed by H. Green.[5] This phenomenon has deep significance in connection with the theory of reinforcement.[6]

MECHANICAL PROPERTIES

The physical testing of rubber has been actively carried on but with no important contributions to testing technic.[7] Standardization as to equipment, procedure, and representation is beginning to receive the attention it deserves.[8]

STRESS-STRAIN CURVE—The attention of rubber workers continues to be directed less toward breaking values and more toward the complete curve. The "conchoid" analogy of Schidrowitz and Goldsborough has been shown to be inadequate,[9] and Shields,[10] and somewhat later, Hatschek,[11] have published new formulas based on curves distorted by calculation to actual cross section; the former, who seems to use only the early part of the curve, arriving at a complex logarithmic expression, the latter deriving in elegant fashion a rectangular hyperbola for the same curve. The present writer finds that when the Hatschek method is applied to curves for stocks representing a range of typical factory mixings the construction is inapplicable. Moreover, neither author has established any physical significance for the parameters that appear in their equations.

Vogt[12] has described a modified method of recording stress-strain data, which facilitates the closer study of reversion phenomena.

ENERGY RELATIONSHIPS—Of the many physical constants [illegible] perhaps the most comprehensive single index is the energy of resilience [illegible] curve on the elongation axis. Proposed in June 1920,[13] this quantity has been widely adopted. Gurney and Tavener[14] describe the energy absorption of various mixings subjected to repeated stresses, emphasizing the superiority of high-rubber compounds for work (such as in airplanes) requiring a slow rate of energy absorption. An important application to automotive equipment is the use of rubber spring shackles.[15] Hysteresis losses, as influenced by cure, pigment loading, and cyclic elongation, are described by Wiegand.[16]

An interesting fact is the very large increase in resilience induced by the addition of a highly dispersed nonelastic phase such as carbon black.

VOLUME CHANGES—The outstanding contribution is H. F. Schippel's[4] paper showing the enormous increases in volume (as much as 100 per cent) when highly pigmented stocks are strained. This has a vital bearing on elastic theory. Sanderson[17] has studied the thermal expansion of various mixings, finding no discontinuity at the vulcanizing point.

GRAIN—Van Rossem[18] has described calender grain, including its disappearance through heating, which he assigns to the Joule effect. In this opinion he is opposed by Wiegand[19] and Lunn[3] who regard the phenomenon as essentially due to viscosity-temperature relationships. (See also Skellon.[20])

Hardness tests have been thoroughly studied by Gurney,[21] particularly as applied to the manufacture of rubber-covered rolls.

EFFECT OF COMPOUNDING INGREDIENTS—The connection between fineness of subdivision and reinforcing action has been definitely established.[2,6] Further work is necessary to clear up the rôle played by adhesional forces as distinguished from specific surface. The mechanical properties of vulcanized rubber have been shown to be controllable over very wide ranges through the intelligent use of various fillers. The remarkable reinforcing properties of carbonate of magnesium have been well established by Greider.[22] Mineral rubber has been the subject of a masterly study by C. O. North.[23]

The important bearing of particle shape upon the phenomena of grain, set, and hysteresis demands further study.[24]

MEASUREMENT OF PARTICLE SIZE—The importance of subdivision as a guide to pigment reinforcement has stimulated H. Green[25] to develop to great precision the direct microscopic method. Using violet light, this worker has been able to measure particles down to 0.2 micron in diameter. H. A. Gardner[26] has described a very novel method of estimating the fineness and texture of pigments by rubbing them on a phonograph record. W. W. Vogt[27] favors the obscurometer method of measuring average particle size. This has had strong criticism from the standpoint of refractive index.[28]

Those who favor clay as a compounding ingredient will find the paper by Comber[29] very suggestive.

The race for superfine rubber pigments has led to intensive research, working both from the atomic state (sublimed litharge, zinc oxide, magnesium carbonate), and from the coarse condition.[30]

Thus we may soon come upon the ideal pigment, one which unites colloidal fineness with freedom from entrained air and is at the same time light, cheap, and easily dispersed on the mill. The production of such an ingredient in the standard colors will mark a new era in rubber compounding.

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* Numbers in text [illegible] paper.

Physical Effects of Accelerators—Reinforcement is, however, attainable by means other than the introduction of a highly dispersed phase. The organic accelerators, besides shortening the cure, greatly improve the mechanical properties. Schidrowitz and Burnand[31] have shown that piperidine piperidyldithiocarbamate increases energy of resilience and ultimate tensile and decreases (improves) the "slope"—facts well known in the art.

Lack of space precludes detailed reference to other papers bearing on the physical aspects of acceleration.[32] Especial importance, however, attaches to the scholarly work of Twiss and his collaborators in which, *inter alia*, is described the interesting pseudo-reversion of accelerated mixings containing only small percentages of zinc oxide.

Other Physical Properties—The thermal conductivity of rubber and the more common ingredients has rightly attracted attention, and during the period under review two papers have appeared, Somerville,[33] and Williams.[34] The results arrived at by these two workers differ so radically as to leave the reader in complete ignorance. The subject deserves clearing up.

Hitherto the reversible heat (Joule effect) involved in deformations has been left entirely unrecognized in physical testing. Isothermal or nearly isothermal conditions have been chosen, whereas service conditions (as in tires) are in many cases adiabatic.

Thus the present writer feels that rubber deserves better from the thermodynamicians, and looks to the day when a Willard Gibbs or a van't Hoff will formulate for rubber the laws so carefully worked out for gases and solutions. In this connection the impact test (by Schob pendulum, for example) offers possibilities for adiabatic research.

The physical conditions attending the action of light on rubber have been carefully studied by Porritt.[35,36] An interesting commercial development is the "Rubber Glass,"[37] being developed by Fordyce Jones by means of the Peachey cure. It will be interesting to observe the light aging properties of this substance.

The variability of crude rubber as regards cure is becoming relatively less important than its variability as regards milling properties and behavior in cements. We hope for more papers on this problem. The difficulty has been to develop clear-cut technic for the quantitative expression of these differences.

Permeability to gases has been carefully studied by Edwards and Pickering.[38] Accelerated heat aging tests have become a definite part of testing technic, owing chiefly to the work of Dr. W. C. Geer.[39]

It is to be hoped that an increasing number of graduate physicists will be attracted to rubber, a subject in which they will find ample scope for work of the greatest theoretical as well as practical importance.

References

1—Green, *J. Ind. Eng. Chem.*, **13** (1921), 1130; *Ibid.*, **12** (1920), 1156.

2—North, *Rubber Age*, **7** (1920), 461.

3—Lunn, *India Rubber J.*, **42** (1921), 831.

4—Schippel, *J. Ind. Eng. Chem.*, **12** (1922), 33.

5—Green, *Ibid.*, **13** (1921), 1029.

6—Wiegand, *Can. Chem. J.*, **1920**, 160; Geer, *J. Ind. Eng. Chem.*, **14** (1922), 369.

7—*Gummi-Ztg.*, **34** (1920), 995; *Rubber Age*, **3** (1917), 57.

8—*U. S. Bur. Stds., Circ.* **38**, September 28, **1921**; Schidrowitz, *India Rubber J.*, **60** (1920), 36; Van Rossem, *Kolloidchem. Beihefte*, **12** (1920), 103.

9—Wiegand, *Can. Chem. J.*, **4** (1920), 160; De Vries, *J. Soc. Chem. Ind.*, **39** (1920), 308T; T. Stevens, *Bull. Rubber Growers Assoc.*, **3** (1921), 246.

10—Shields, *Rubber Age*, **10** (1920), 88.

11—Hatschek, *J. Soc. Chem. Ind.*, **40** (1920), 251T.

12—Vogt, *India Rubber World*, **66** (1922), 421.

13—Wiegand, *Can. Chem. J.*, **4** (1920), 160.

14—Gurney and Tavener, *J. Ind. Eng. Chem.*, **14** (1922), 131.

15—"Rubber Shock Insulators for Busses," *India Rubber World*, **64** (1921), 115.

16—Wiegand, *J. Ind. Eng. Chem.*, **13** (1921), 118.

17—Sanderson, *India Rubber J.*, **59** (1920), 305.

18—Van Rossem, *Ibid.*, **62** (1921), 343.

19—Wiegand, *Ibid.*, **62** (1921), 733.

20—Skellon, *Rubber Age*, **1** (1921), 546.

21—Gurney, *J. Ind. Eng. Chem.*, **13** (1921), 707.

22—H. W. Greider, *Ibid.*, **14** (1922), 385.

23—North, *Rubber Age*, **10** (1922), 130.

24—Greider, *Ibid.*, **10** (1922), 159.

25—Green, *J. Frank. Inst.*, **192** (1921), 637.

26—Gardner, *Paint Mfrs. Assoc., U. S. Educational Bur., Circ.* **90**.

27—Vogt, *India Rubber World*, **66** (1922), 347; see also Lawny, *Chem. Age (London)*, **6** (1922), 344.

28—Feldenheimer, *Rubber Age*, **10** (1922), 8.

29—Comber, *J. Soc. Chem. Ind.*, **41** (1922), 77T.

30—Ginsberg, *Rubber Age*, **10** (1922), 325.

31—Schidrowitz and Burnand, *J. Soc. Chem. Ind.*, **40** (1921), 269T.

32—Maximoff, *Rubber Age*, **9** (1921), 11, 53; Kratz and Flower, *J. Ind. Eng. Chem.*, **13** (1921), 971; Kratz, Flower and Shapiro, *Ibid.*, **13** (1921), 128; Whitby and Walker, *Ibid.*, **13** (1921), 816; De Vries, *Ibid.*, **13** (1921), 1133; Schidrowitz, *India Rubber J.*, **61** (1921), 731; Twiss and Brazier, *J. Soc. Chem. Ind.*, **33** (1920), 125T, 155T; Twiss and Howson, *Ibid.*, **39** (1920), 287; Twiss and Thomas, *Ibid.*, **40** (1921), 49T; Twiss, Brazier and Thomas, *Ibid.*, **41** (1922), 81T; Endres, *Le Caoutchouc et la gutta percha*, **18** (1921), 11089; Spoon, *Ibid.*, **18** (1921), 10831.

33—Somerville, *Chem. Met. Eng.*, **24** (1921), 834.

34—Williams, *India Rubber J.*, **43** (1922), 890.

35—Porritt, *Ibid.*, **60** (1920), 21.

36—Lewis and Porritt, *J. Soc. Chem. Ind.*, **40** (1921), 18T.

37—Fordyce Jones, *India Rubber Rev.*, **1922**, 39.

38—Edwards and Pickering, *Chem. Met. Eng.*, **23** (1920), 17, 71.

39—Geer and Evans, *India Rubber J.*, **61** (1921), 35.

Fatal Explosion at Harvard College

On May 19, 1922, an explosion and fire occurred at the Jefferson Physical Laboratory at Harvard College, which was fatal to two and injured several others.

According to the evidence, Mr. A. K. Dunbar, one of those killed, was compressing oxygen from a balloon situated just outside of the building into a steel gas cylinder that was standing on the cement floor of the basement. Compression was effected by means of a Whitehead, two-stage compressor with water-lubricated cylinders, of about one-half cubic foot per minute capacity, driven by an electric motor. The gas, after passing through the two stages of the compressor, was conducted through a small water separator and thence into the cylinder where, at the time of the explosion, it had reached approximately 1500 lbs. per square inch.

Mr. Dunbar was in an adjoining room conducting gas analyses and hastened to the compressor upon hearing a slight pop in the safety valve. The motor had stopped and he went to the main switchboard to ascertain the cause, after which he returned to the compressor room, started the compressor, and was evidently standing near the apparatus when the explosion occurred.

The primary explosion was evidently in the lower part of the steel cylinder into which the gas was being compressed, and the flying fragments exploded the separator and a partly filled cylinder of illuminating gas. The probable cause of the explosion was oxygen gas under high pressure coming in contact with oil in the lower part of the cylinder.

In the compression of hydrogen gas into steel cylinders, oil is used for lubrication, some of which finds its way into the cylinder or upon the valve thereof. In compressing oxygen gas, water or soapy water is used for lubrication, since whenever oil comes in contact with oxygen under high pressures an explosion generally follows. To avoid such accidental explosions, all cylinders used for hydrogen compression are fitted with screw connections having left-hand threads. The cylinder that exploded had a left-handed connection, and the evidence seems to show that at some previous time it had been used for the storage of hydrogen under pressure, and probably contained oil which caused the explosion.

It is reported that a new process for making colored motion pictures has been perfected by the Technicolor, Inc., of which William Hamlin Childs is the head. A plant is to be built near New York with a capacity of 1,000,000 ft. of film weekly.

The Chemistry of Rubber Vulcanization and Acceleration

By C. W. Bedford

Research Laboratories, The B. F. Goodrich Co., Akron, Ohio

IT IS NOW generally conceded that the vulcanization of rubber is a chemical process, while physical chemistry plays a secondary, although important part. The addition of sulfur to rubber has long been recognized as greatly facilitated by the presence of inorganic accelerators such as litharge, lime or white lead, the latter having been first used by Charles Goodyear himself, but only within the past few years has it been shown that these inorganic accelerators are dependent on the presence of resins, proteins, organic accelerators or other organic substances, and that their action is secondary in character. While the accelerating action of ammonia had been observed in 1881,[1] it was not until 1906 that the organic nitrogenous accelerator was discovered. Since the publication of the Bayer patents on piperidine in 1912 the number of known organic accelerators has increased into the hundreds.

The mechanism of the vulcanization process is each year becoming more fully understood through the efforts of rubber chemists the world over. The following is a brief summary of the results of their latest work.

C. W. Bedford

The relative reactivity of different forms of sulfur is a fundamental question which has recently been investigated further by D. F. Twiss.[2] His work indicates that there is little difference in activity between soluble and insoluble sulfur at temperatures from 68° to 188° C. The Peachey process of vulcanization by hydrogen sulfide and sulfur dioxide[3] gases at ordinary temperatures liberates a form of sulfur which may be isolated[4] and used for vulcanizing rubber at low temperatures. This form of sulfur quickly changes through the insoluble or plastic variety to ordinary rhombic sulfur, thereby losing its extraordinary vulcanizing power. The question of "nascent" sulfur and its possible reaction with rubber is still an open one. Peachey has relied on this explanation for his cold vulcanization by gases. Others have called attention to the inactivity of nascent sulfur liberated in rubber cements by the action of hydrogen sulfide on aromatic nitroso compounds.[4] This question is of great importance for the ultimate explanation of the mechanism of vulcanization.

Vulcanization by organic disulfides without the use of elemental sulfur has recently been reported from several sources. Romani[5] cites tetramethyl thiuram disulfide and Caldwell[6] mentions oxybutyl thiocarbonic disulfide (butyl [illegible] [illegible]lfide). The disulfides are said to revert to [illegible] giving up the other atom of sulfur to the rubber. [illegible] previously vulcanized rubber with hydrogen disulfide, and Kratz[8] used ammonium hydrosulfide without free sulfur but in the presence of air (ammonium disulfide). Vulcanization with disulfides seems to be related to the vulcanization without sulfur by benzoyl and other peroxides, according to Ostromuislenskii.[9]

Closely related to the action of disulfides is the action of higher polysulfides. The use of antimony persulfides is well known. Gerard vulcanized with zinc[12] and calcium polysulfides,[10] Bourquin[11] used the polysulfides of hydrogen, sodium, and calcium, Esch[12] worked with magnesium polysulfide, and C. O. Weber[13] states that zinc sulfide has some vulcanizing action. Erdmann,[14] in 1908, proposed a polysulfide theory of vulcanization through the formation of thiozonides, a theory that was later expanded by Ostromuislenskii,[15] Kratz,[16] Bedford,[17] Bruni,[18] and their co-workers. Organic polysulfides of meta-toluylene diamine disulfide, mercapto-benzothiazole disulfide, and other disulfides are also used for vulcanization purposes. Their action, however, is greatly aided by the presence of zinc oxide.

A further advance in rubber chemistry was made by Ostromuislenskii[19] by the discovery of the rapid vulcanization of rubber at ordinary temperatures. The dithiocarbamates of piperidine, methyl amines and many other organic bases cause sulfur to vulcanize rubber at room temperatures in a comparatively short time. Later it was shown that this vulcanizing power is available only in the presence of metallic oxides and that metallic salts of dithiocarbamates function in the process of vulcanization. Ostromuislenskii[20] also found that zinc alkyl xanthates are equally strong in their accelerating power although they contain no nitrogen, an element which for many years was considered necessary for vulcanization. Zinc thiophenols[21] have also been added to the list of nonnitrogenous accelerators.

Most organic accelerators rely on the secondary action of metallic oxides to bring out their full vulcanizing power, while some, such as aniline and aldehyde ammonia, are retarded thereby. Scott and Bedford[17] have divided organic accelerators into two classes: (*a*) hydrogen sulfide polysulfide accelerators, (*b*) carbosulfhydryl polysulfide accelerators. The first class includes compounds such as aniline which do not need the aid of inorganic accelerators, and are supposed to form polysulfides by first reacting with hydrogen sulfide to form derivatives of ammonium sulfide, then dissolving sulfur to form polysulfides similar to ammonium poly-

[1] [illegible]

[2] [illegible]

[3] [illegible]

[4] [illegible]

[5] [illegible] 16 [illegible]

[6] [illegible]

[7] [illegible]

[8] [illegible] 13 [illegible]

[9] U. S. Patent 1,249,181 (1917).

[10] Gmelin, "Handbook of Chemistry," **17**, 349.

[11] *Gummi Markt.*, **4** (1910), 408.

[12] *Ibid.*, **9**, 68 and 125

[13] *Z. angew. Chem.*, **1893**, 631, 661.

[14] *Ann.*, **362** (1908), 133.

[15] *C. A.*, **10** (1916), 1944, 3177.

[16] This Journal, **12** (1920), 317

[17] *Ibid.*, **13** (1921), 125.

[18] *C. A.*, **15** (1921), 3915.

[19] *Ibid.*, **10** (1916), 1943.

[20] *Ibid.*, **10** (1916), 3176.

[21] This Journal, **13** (1921), 1034

sulfide. The second class either contains carbosulfhydryl groups or forms them by reactions during vulcanization. This class includes mercaptans, dithiocarbamates, thioureas, xanthates, etc., and is said to function through the formation of the metallic salts which are described as forming mercaptide polysulfides that contain per-sulfur sufficiently active to react with rubber at ordinary temperatures. In support of this general theory there has been prepared an active type of zinc sulfide[4] which forms polysulfides and is an active accelerator. Thiocarbanilide is comparatively inactive in the absence of zinc oxide and has been found to form zinc and lead mercaptides through its tautomeric mercapto form.

Twiss[21] energetically disagrees with this theory of the action of zinc mercaptides, dithiocarbamates, xanthates, etc., calling attention to the fact that the zinc salts still need the presence of zinc oxide to bring out their full vulcanizing power. Bedford and Sebrell[22] found that their action was also increased, in rubber cements, by the presence of aniline, and Cadwell[6, 22] finds the same action of aniline and other amines, not only on zinc dithiocarbamates, xanthates, etc., but also on thiuram disulfides and xanthic disulfides:

$$(R_2N—CS—S—S—CS—NR_2 \text{ and } RO—CS—S—SCS—OR)$$

Bruni[18] offers a second theory for the action of zinc oxide, which parallels the above-mentioned theory up to the formation of the zinc salt of the thio acid or mercaptan. He states that sulfur reacts with the zinc salt to form a disulfide and zinc sulfide according to the equation:

$$(R_2N—CS—S—)_2 Zn + S = (R_2N—CS—S)_2 + ZnS$$

This disulfide is then believed to vulcanize the rubber by reverting to the monosulfide, which in turn reacts with elemental sulfur to reform the disulfide. Twiss[23] again calls attention to the need of zinc oxide for bringing out the full effect of the disulfide, even when the disulfide is formed outside the rubber mix and compounded as such, under which conditions Bruni's theoretical need or zinc oxide should be absent. Twiss believes that there is some reaction product common to disulfides, dithiocarbamates, zinc oxide, and sulfur, which forms the true accelerator or vulcanizing agent.

Further in regard to the thiuram disulfides, it has been shown that they do not vulcanize rubber-sulfur-zinc oxide mixes at room temperature as do the zinc salts described below, while the action of hydrogen sulfide,[4] even at ordinary temperatures, changes the disulfide to a dithiocarbamate, and in the presence of zinc oxide starts the process of rapid vulcanization without the application of heat. The above-mentioned action of aniline in causing thiuram disulfides to vulcanize rubber at ordinary temperatures may be explained in the same manner according to Fromm[24] who showed that aniline and other primary amines easily react with these disulfides to form dithiocarbamates. Thiuram disulfides as well as dithiocarbamates, derived from secondary amines, are found by Twiss to be much more active than those from primary amines.

In general, the study of the mechanism of vulcanization seems to be concentrating on the action of accelerators which need the aid of zinc oxide. Little has been published on the effect of litharge, lime or magnesia. The action of aniline, aldehyde ammonia, para nitroso-dimethyl aniline, and many other accelerators still remains practically untouched. The important factor of temperature, the nonactivity of certain accelerators at temperatures where others are violently active, has been commented on as due to the relative stability or instability of the reaction products, but a satisfactory explanation has not yet appeared.

This, in brief, is the present status of the chemistry of rubber vulcanization. The advent of the organic accelerator has furnished the rubber chemist definite chemical compounds for use in vulcanization and provided a means of throwing some light on the mechanism of the process. In general, the polysulfide theory is fairly well accepted; in detail there are many differences of opinion and many unsolved problems. History, in connection with rubber chemistry, is being made at a rapid rate and we await with extreme interest the developments of the immediate future.

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[22] Brit. Patent Application 177,493 (1922).

[23] *J. Soc. Chem. Ind.*, **61** (1922), 81T.

[24] *Ann.*, **348**, 144.

D. H. Killeffer Succeeds R. T. Stokes

Following the sudden death of the former secretary of the Biscuit and Cracker Manufacturers' Association, the position was offered to and accepted by Mr. R. T. Stokes who had but recently become associate editor of THIS JOURNAL.

Mr. D. H. Killeffer has been appointed associate editor to succeed Mr. Stokes. Mr. Killeffer is a graduate of the University of North Carolina. After graduation he became a member of the staff of the Brown Laboratories of Nashville and served in the department of tests of the Nashville, Chattanooga, and St. Louis Railway. Subsequently he was research chemist on plant development for the Calco Chemical Co., and since January 1920 has been a member of the editorial staff of Drug and Chemical Markets.

Mr. Killeffer will have headquarters in New York but our readers will meet him frequently in other parts of the country, particularly in industrial chemical fields.

D. H. KILLEFFER

Meeting of Chemists at Utrecht

At Utrecht on June 21 to 23 there was held the first gathering since the war at which chemists from Germany and Austria have met chemists from England, America, and other countries.

America: L. M. Dennis, D. A. MacInnes, W. A. Noyes.
Austria: E. Abel, J. Billiter, F. Emich, A. Kailan, A. Klemenc, F. Pregl, A. Skrabal, R. Wegecheider.
Czechoslovakia: J. V. Dubsky, A. Simek.
Denmark: N. B. Bjerrum, J. N. Brönsted, J. Petersen, Chr. Winther.
England: E. C. C. Baly, F. G. Donnan, W. C. McLewis.
Germany: M. Bodenstein, G. Bredig, O. Hahn, P. Pfeiffer, R. Schenck, W. Schlenck, A. Stock, P. Walden, H. Wieland.
Holland: J. Backer, J. J. Blansma, Ernst Cohen, A. F. Holleman, F. M. Jaeger, H. R. Kruyt, W. Reinders, P. van Romburg.
Lithuania: M. Centnerschwer. *Russia:* N. Schilow. *Switzerland:* J. Piccard.

The original suggestion of the meeting was made by Professor Donnan of London, and the preliminary plans were made at a meeting in the home of Professor Cohen of Utrecht in June 1921. The details were carried out by Professor Cohen.

The following scientific papers were read and discussed:

E. C. C. BALY. **Photochemical Catalysis.**
P. WALDEN. **Free Radicals.**
W. A. NOYES. **Positive and Negative Valences.**
W. SCHLENCK. **Contributions to the Chemistry of Free Radicals and the Varying Affinity of Carbon Compounds.**
M. BODENSTEIN. **The Photochemical Structure of Phosgene.**
L. M. DENNIS. **The Preparation and Properties of Metallic Germanium.**
H. WIELAND. **Free Radicals.**
N. SCHILOW. **Distribution Equilibria.**
J. PICCARD. **Absorption Colors of the Second Class.**
E. ABEL. **Direct and Indirect Esterification in Absolute and Aqueous Glycerol, According to Experiments of Karl Heidrich.**
A. KLEMENC. **Vapor Pressures of Isometric Benzol Derivatives.**
M. CENTNERSCHWER. **A Proposal for the Introduction of a Small Unit of Measure (Radion).**

At a reception in Hotel Pays-Bas on Wednesday afternoon, there were addresses of welcome by G. L. Voerman, President of the Chemical Society of Holland; Professor Went, President of the Royal Academy of Science of Amsterdam, and a response by W. A. Noyes. [*W. A. Noyes*, Urbana, Ill.]

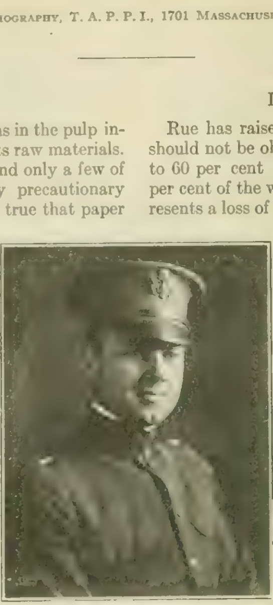
Recent Advances in Pulp and Paper

By Clarence J. West

Chairman, Committee on Bibliography, T. A. P. P. I., 1701 Massachusetts Ave., Washington, D. C.

Raw Materials

One of the most interesting questions in the pulp industry to-day is the future source of its raw materials. The forests are rapidly disappearing and only a few of the more enterprising mills are taking any precautionary measures with regard to reforestation. It is true that paper can be made from practically any fibrous material known, but it is also true that, in the majority of such raw materials, the process is far from being satisfactory, as far as the yield of pulp is concerned. It is not possible, in the United States at least, to prepare pulp from annual plants and similar materials, under conditions that make the process economically feasible.



C. J. West

The most promising raw materials, other than wood, thus far studied are bamboo and cotton linters. The early difficulties encountered in the treatment of bamboo have now been overcome and one or two methods are known to be quite successful.

India appears to offer an inexhaustible supply. According to Raitt, India, with its supply of bamboo, and the Savannah grasses, can produce pulp for the whole world. Raitt further estimates that the cost of production of bamboo pulp would not exceed half that of the manufacture of wood pulp. Many years ago the Department of Agriculture tried to cultivate bamboo in the southern states, but their experiments were not very successful. It still remains to determine whether bamboo can be grown in this country. If so, this would offer one solution of the problem of raw materials.

Cotton linter pulp has attracted much attention since the war. The great demand for cotton during the war period made it necessary that the cotton attached to the seed after the usual ginning process (about 200 lbs. to the ton of seed) be removed as far as possible. At the conclusion of the war the demand for this material dropped practically to zero, and successful efforts were made to convert this into pulp for paper. The manufacturers claim that this pulp may be used to advantage in place of old rags, and also in certain proportions in place of new rags. Because it is a new cotton fiber which has not been worked or processed, it gives somewhat greater bulk to paper for the same unit of weight. There is, naturally, still some question in the minds of certain paper manufacturers as to how far this pulp will be successful, but it is felt that it can be mixed with other pulps even if it cannot be used alone.

Papyrus has been proved as a paper-making material but the source of supply (Zululand and the Sudan, as well as other parts of Africa) would seem to make it unimportant as a raw material for American manufacture.

Processes have been developed for utilizing the Jack pine, which will make available large tracts of this hitherto little-used species. Very interesting developments are reported along the line of the use of southern pine waste. Some of the claims of the promoters are questioned and only large-scale operations can settle the question.

Improvements in Processes

Rue has raised the question why a greater yield of pulp should not be obtained in the chemical processes. Fifty-five to 60 per cent of wood is true cellulose, yet less than 45 per cent of the wood is obtained as high-grade pulp; this represents a loss of about 25 per cent. The solution of the problem will necessitate a fundamental research into the various processes of pulping wood. The further need of economical utilization of other woods than spruce, hemlock, and balsam fir is also a pressing problem.

The Forest Products Laboratory has suggested that one solution of these problems may be obtained through a preliminary impregnation of the wood before digestion. The initial results indicate an appreciably shorter cooking time at lower temperatures. It is probable that the method will require a change in the usual acid composition to take care of the increased speed of the chemical reaction. The results will be increased yield, decreased screenings, and stronger pulp. Another innovation in digesting practice consists in fractional digestion, introduced by Aitken in the cooking of esparto. He proposes to remove members of the starch and pectose groups in the first treatment, using a 1.5 per cent sodium hydroxide solution, and then remove the ligneous material by a more drastic treatment with 14 per cent alkali. This method gives a cleaner and more easily washed stock, greater economy of bleach and reduction in costs of recovery. No mention has been made of comparative yields.

The process of rag boiling has been studied by Grimm. It is stated that the mechanical treatment to which the stock is subjected in the washer and in the hollander modifies the chemical constituents of the fibers very considerably. His conclusion is that the present proportion of chemicals and rags is correct. This is the first time the commercial practice has been checked by scientific studies in the laboratory.

The possibility of using decayed pulp wood has been studied by Bates and by Sutermeister. Bates concludes that infected wood may be used for sulfite pulp production if decay is limited to discoloration, and believes that chipper dust pulp might be satisfactorily blended with ordinary sulfite pulp and so utilized. Sutermeister has found that by using wood permeated with threads of dry rot but still quite hard and firm, the yield was considerably lower, the fiber weaker and practically unbleachable. Stained wood had little effect upon any quality other than that of bleaching. Bleach consumption in the case of stained pulp was about 15 per cent as compared with 10 per cent for an ordinary pulp.

Analytical Methods

Methods of control in the pulp mill continue to be a subject of investigation. Various analytical methods for sulfite liquors have been proposed and reviewed. While the analysis of the raw acid seems to be a comparatively simple one, the analysis of the liquor produced during the digestion of the wood is complicated by the presence of the decomposition products from the ligneous portions of the wood, and the analysis of the sulfite waste liquor seems an almost hopeless task.

Another interesting field of research is in methods of differentiating the various pulps, sulfite, sulfate, soda, and mechanical. The whole procedure, from the preparation of standard samples of known pulps to the actual determination of the composition of unknown mixtures, is in need of standardization. Various stains have been proposed for this purpose but it seems a difficult matter to obtain a sufficiently marked differential staining of some of the pulps to enable even an approximately accurate determination. Lofton and Merritt have recently proposed the use of Malachite Green and Basic Fuchsin for determining the amounts of unbleached sulfite and sulfate pulps in a mixture of the two. The sulfate fibers are stained a blue or blue-green while the sulfite fibers assume a purple or pink color.

The need of standard methods is thoroughly recognized by the Technical Association of the Pulp and Paper Industry, which has a committee actively engaged in the preparation of a set of methods which it is hoped will prove so satisfactory that they will be adopted by the whole industry.

Beating

The most important questions in the beating of paper pulp are methods of accelerating the process, thereby decreasing the cost and methods for the control of the process. It is believed that a possible improvement in the manner of beating consists in the use of higher concentrations of stock moving through the beater at a higher rate of speed. This suggests that it is not the length of time which the stock is in contact with the water in the beater but the total distance that the stock travels that determines the degree of beating. The question of chemical hydration of pulp has been discussed by McKay. He claims that the process introduced by Meigs, Bassett and Slaughter will give an increase in strength of the finished sheet with no reduction in the paper-making qualities of the pulp, a decrease in beating time and a reduction in caustic, time of digestion, amount of bleach, and time required for bleaching with every grade of stock. One of the most interesting parts of McKay's contribution is the fact that he has introduced the copper number and viscosity as means of controlling the degree of beating. Much more work is necessary before it can be said that these methods will or will not answer the problem of control. It does seem to be certain that the so-called slowness test does not.

Bleaching

The bleaching of paper pulp, in the case of rags, may be readily carried out by the use of liquid chlorine. In this process no special equipment is necessary, for the liquid chlorine may be injected directly into the beater or washer where the bleaching is done. This avoids the handling of bleach drums and solutions and tends to cleanliness in the mill. The only danger is from the fumes of chlorine gas, and with properly designed control apparatus this should be very slight. The use of liquid chlorine is, it is believed, gradually displacing the electrolytic bleach in many paper mills. Because of the higher concentrations necessary, it is not possible to use liquid chlorine with chemical pulp as in the case of rags. It is first transformed into calcium hypochlorite solution, which solution is claimed to have quite different physical properties from that prepared from dry bleaching powder. Much of the success of this application depends upon the apparatus developed by the Wallace and Tiernan Company for controlling liquid chlorine. This makes possible the production of an absolutely uniform liquor. This liquor has a lower alkalinity than that prepared from bleaching powder which, under some conditions at least, is an advantage.

Wolff has proposed a new form of bleaching tub which permits the circulation of pulp concentrations of 10 to 15 per cent; naturally this gives a greater efficiency of operation. An important advantage is the saving of steam in bleaching at lower temperatures, while there is also less loss of fiber and cleaner pulp.

Wells has studied the bleaching of soda and sulfate pulps, prepared from coniferous woods, by the action of bleaching powder solutions. He finds that the alkali-solubility of the pulps increases with the strength of bleaching liquor employed and that considerable degradation of the cellulose takes place before the color is removed, indicating the unsatisfactory nature of this type of bleach. He obtains slightly more satisfactory results with regard to color removal by carrying out the bleach treatment in two stages with an intermediate washing. The pentosan contents of the pulps were found to be unaffected by bleaching, but on the other hand their methoxyl contents were reduced by the treatment.

Sizing

Little advance has been made in the study of sizing materials. The most important study is that of Blasweiler on the use of water glass (sodium silicate). He made a large number of tests with water glass alone and in combination with soaps, fats, animal size, starch, casein, etc. He draws the following conclusions, which may or may not be warranted: good suction on the paper machines; no sticking at the press rolls; rapid and complete setting of the suspended matter in backwater; greater strength and better rattle to the paper with a higher retention of clay or loadings; good color and dyeing results. Vail has also discussed, in various trade journals, the uses of water glass in the paper industry.

One of the interesting questions of the present day is the difference between gum and wood rosin in the sizing of paper, and especially in the color imparted by the latter. That there is a difference even the manufacturers of wood rosin admit. We have still to discover the reason and to remedy it, if possible.

Another question that is engaging the attention of some of the technical men of the industry is that of the real meaning of sizing quality of paper and a method of measuring it in terms of a definite, absolute unit. There are many tests for sizing quality. Recently the Valley Size Tester has appeared. This machine claims to give an accurate unit for sizing and to enable the manufacturer to keep his sizing constant during a run and from run to run. The test, however, is a relative one, and does not give us a fundamental unit for sizing quality. Such a unit is really necessary before a careful study of the factors influencing the sizing quality of paper can be made. The Paper Section of the Bureau of Standards is studying the general question of the testing of the sizing and it is hoped that they may be able to solve the problems involved.

Much interest has been aroused in the announcement of the Englishman, Kaye, that the application of rubber latex to paper-making appears to improve the texture and the strength of the paper so treated. The paper possesses the property of folding without serious permanent cracking along the line of fold. It is also claimed to be more water-repellent than paper not treated with rubber. Many other claims are made, based in part on commercial tests. If these results are substantiated by other mills, it would seem that this was an important contribution to the industry.

The Flintkote Company has reported a process for the emulsification of asphalt by means of a highly colloidal clay, so that it may be introduced into the paper-making process [illegible] paper machine. By the use of this [illegible] waterproof or moisture-proof boards of various stiffness or pliability. The results with this method give a higher degree of resistance to water than results when raw paper or felt is saturated in a bath of hot asphalt, in accordance with the usual practice obtaining in a saturating plant.

. . . . .

This brief review indicates that the pulp and paper industry is not without its own problems. Many others purely mechanical and having no place here, also confront it. The depression of the past two years has made progress in the solution of these problems almost impossible. It is anticipated, however, that the coming years will see the proper recognition of the place of the technical man in the industry and that many changes, some of them almost revolutionary in character, will be made, which will increase the efficiency of the various processes, conserve our raw materials, and give us an improved product. Not the least of these advances, we hope, will be the adoption of the standardization program now being developed through the coöperation of the manufacturers of paper with the Paper Section of the Bureau of Standards.

Hardwood Distillation

By **Harry C. Merriam**

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H. C. MERRIAM

THE HARDWOOD distillation industry is carried on in the United States by 80 different concerns, operating 93 plants, with a total daily capacity of 5530 cords, 600 of which are in by-product recovery kilns and 4930 cords in ovens and retorts.

During the last ten years great progress has been made in the methods employed in the wood distillation industry, and it is the object of this paper to touch upon the most important.

Ovens have practically replaced smaller retort types and the tendency of the modern plant is toward large units. The largest oven plant operates twenty-two 10-cord ovens, with a total capacity of 220 cords, which can be increased to practically 294 cords per day on a carbonization period of 18 hours.

The larger plants are used in conjunction with charcoal pig-iron blast furnaces and it is on this account that such large units are desirable. Most of these plants are situated in Michigan, although during the war four were built in the south.

The obtaining of sufficient quantities of cord wood has always been one of the vital problems of the wood distillation plant. During the recent war, with the scarcity of labor, this factor was very pronounced, and made most manufacturers abandon the cutting of cord wood in the woods and ship the logs direct to the plant, where they were handled in a sawmill. Some of the original sawmills were cumbersome and costly, but modifications and improvements have been carried out so that to-day the wood mill of a modern wood distillation plant will supply at reasonable cost wood suitable for distillation purposes. It has, moreover, been found fairly easy to procure log-wood cutters when previously cord-wood cutters could not be obtained.

The green logs are brought directly to the wood distillation plant, put through the wood mill, cut into approximately 49-in. lengths, and split with band or circular [illegible] passed through block mills and cut to 12-in. lengths. At this point any [illegible] cut to block. These blocks, freed of sawdust, are elevated to bins and from there dumped by gravity into the retort cars, the sides of which are carried to the top. The cars are then run into the predriers, which are of ordinary tunnel construction, either of reinforced concrete or brick, through which the waste stack gases from the ovens are circulated countercurrent to the wood and in direct contact with it. The driers vary in size, allowing from one to three carbonizing periods for drying. The two-period drying is now considered good practice.

Savings effected by this system include: decreased labor due to the mechanical handling of the wood; interest on the investment in cord wood in the drying yards; insurance, taxes, etc.; decrease in fuel consumption, with the advantage of uniformity in the character of wood entering the ovens under all weather conditions; an increase in the output of the plant by shortening the carbonization period; and the elimination of brands from the charcoal.

The application of strict temperature control to the ovens has been recognized as of great importance, and the installation of recording pyrometers for accurate control has resulted. This control not only stabilizes the yields of by-products and increases them in many plants, but prevents the overheating of the ovens, thereby eliminating in large measure the replacement of burned bottoms and costly repairs to the oven settings. It also assures the turning of the ovens in the proper cycle of time, this being a most important factor where the charcoal is used directly in a blast furnace requiring a constant supply.

The importance of large scrubbers for the efficient scrubbing of the retort and kiln gases previous to burning of the same has finally been recognized, and scrubbers of adequate size are now a standard installation in many plants.

In retort practice it has been found that approximately 1 gal. of 82 per cent of alcohol per cord of wood can be recovered, and in the case of kilns where a much larger volume of gas has to be handled, due to air leakage, etc., around the kiln, an increase in yield of from 2 to 3 gal. per cord has been reported. In fact, one kiln plant by efficient scrubbing has obtained an alcohol yield very close to that of the ordinary oven plant.

The distillation of hardwood chips, sawdust, etc., has occasioned considerable research work to develop a successful commercial process. The difficulties encountered, such as in the drying of this waste, because of its own insulating qualities, the control during exothermic reaction, charcoal dust during decomposition, the stabilizing of the fine charcoal so that it will not ignite spontaneously, and the final briquetting of the charcoal, have all been trying problems.

A number of patents have been taken out in conjunction with this work. Three plants have been built on a commercial scale carrying out the various ideas, but only one of these plants, using the Stafford process, has proved a success.

The principle of this process makes use of the hitherto known, but not commercially utilized, heat of exothermic reaction of cellulose when at the carbonizing temperature. By predrying and preheating the material, and introducing it into a retort in which material already undergoing carbonization is present, the exothermic heat is sufficient under properly maintained conditions to bring the additional material up to the carbonizing point, when this material in turn will be carbonized and liberate heat, which will serve to bring further material to the carbonizing temperature. The Stafford process requires no heating of the retort; in fact, the retort is thoroughly lagged to prevent escape of heat. The material is previously dried in contact with the air, and is introduced continuously into the retort from which the charcoal is also continuously removed.

The continuous distillation of hardwood waste produces the same yields in methanol and charcoal and about 50 per cent more in acetic acid than the yields from ovens utilizing cord wood of similar species.

The drying of the wood to a 1 per cent or 2 per cent moisture content is carried out in large rotary driers in direct contact with the hot flue gases, and efficient drying of the wood is thus accomplished. The pyroligneous acid obtained from this dried wood is therefore in a concentrated form and subsequent treatment in the stillhouse is accomplished with a minimum of evaporation and distillation.

The advantages of the mechanical handling of all products, low fuel consumption, large capacity for small units operated continuously, higher yields, etc., make it possible to even hog cord wood and handle in a commercially successful manner. All these advantages point toward the development of this process and a gradual substitution for present practice.

Stillhouse operations have undergone many changes, and to-day the continuous treatment of the pyroligneous acid and other liquors is universally employed in the more modern plants, as against the discontinuous method in the smaller and older type plants.

The use of multiple-effect evaporators has proved a great economy factor. Early designs of multiple-effect evaporators did not take into consideration the fact that when pyroligneous acid is distilled under multiple-effect conditions the vapor on condensing deposits carbon on the surface of the tubes of the next effect, cutting down materially the transmission of heat and necessitating the dismantling of the tube bundles for the removal of the carbon. This fouling of the surface varies with different woods and is more pronounced in the case of southern hardwoods.

The use of triple effects in the evaporation of acetate of lime is a success and gives no particular operating difficulties. It is the consensus of opinion among operators who have used triple effects that double-effect economy in a combination evaporator is all that is desirable in this industry, because of the operating difficulties before mentioned. In the latest designs the pyroligneous acid is evaporated in one effect and the acetate of lime in the other. With proper design this combination gives accessibility to the tube surfaces and permits of the easy removal of the carbon coating without dismantling. Such a double effect gives an easily controlled unit for continuous operation.

In the production of acetate of lime the conversion of the concentrated acetate liquor from the evaporators to the mush state by means of steam-heated rotating rolls, and the final drying of the acetate on screen belt driers traveling in hot waste flue gases, have solved the question of low-cost production of acetate in modern plants and eliminated the troublesome labor problem so often encountered in acetate drying. The elimination of the old acetate pans, which are notorious steam eaters, has been a welcome change.

A recent innovation utilizes the acid vapors from the primary stills as a source of heat in the second effect, operating under a vacuum for the evaporation of acetate of lime liquor, the primary stills being operated under atmospheric conditions and the vapors condensed in separate tube chambers in the second effect. This keeps the distillate from each primary still separate and a visual control of each still is possible. This scheme will undoubtedly result in a considerable saving in steam, and, if adopted by old plants having primary stills, will give double-effect economy.

The application of continuous stills for the production of high-grade crude methanol of around 92 to 95 per cent (Tralles) direct from the neutralized liquor has become the standard practice. Where there is an excess of exhaust steam available, kettles have been eliminated, the steam being introduced directly into the base of the continuous still. This has considerably simplified the apparatus.

The grade of crude alcohol produced in a plant of this type is not to be confused with the crude 82 per cent produced in old plants using older methods.

The use of low pressure steam in the stillhouse has been so perfected that two plants are now operating all of their apparatus, both evaporating and distilling, on 5-lb. pressure exhaust steam.

The successful production of glacial acetic acid from carbide has been a serious blow to the wood distiller, and in his search for some way to meet this menace the production of glacial acetic acid direct from pyroligneous acid has been attempted. It is the writer's understanding that this has been successfully demonstrated on a semicommercial scale. This being so, it will give the distiller a new lease of life by again making his acetic acid a source of income, whereas at present it is a problem to dispose of it, at a profit.

In the past the refining of crude 82 per cent methanol has been carried out in central refineries, because of the difficulties encountered and the type of apparatus necessary. With the advent of the modern four-column continuous refining still, conditions have changed and the crude alcohol producer is enabled to instal his own refining unit and manufacture direct the highest grade of refined methanol. The increasing demand for pure methanol in the dye industry, and particularly in the manufacture of formaldehyde, has caused this type of apparatus to come into its own. Chemical treatment was necessary under the old system to separate the alcohol from last traces of methyl acetone, but with the new type of continuous still this is done by fractionation in the distillation process and pure methanol with a Messinger test of less than $^1/_{20}$ of 1 per cent acetone is produced direct from the crude 82 per cent. There is, too, a simultaneous production of high-grade methyl acetone, together with a small amount of oils and allyl alcohol. The production of pure methanol has enabled many of the smaller plants to instal their own formaldehyde apparatus and by this means place their alcohol on the market converted to its highest value.

The manufacturers of crude alcohol had heretofore only one outlet for their alcohol, namely, the sale of the crude to the refiner. With the modern refinery, he has his choice of a number of markets. In the modern refinery, with its steam regulators, extension stem-recording thermometers, recording pressure gages, and other accessory equipment, one operator can care for a number of stills with more perfect control than was ever possible under the old hand-controlled systems. Furthermore, strict chemical control is possible at all times, and such control is essential because of the chemical specifications that have replaced the old tests, such as odor, color, specific gravity, etc.

The production of pure acetone by the destructive distillation of acetate of lime was worked up to a high degree of efficiency during the war, because of the enormous demand for this product in the manufacture of cordite for the British government, and once again the continuous distillation of the crude acetone into the finished product showed the efficiency and low cost of this method of refining.

In order to meet the recent more stringent requirements for various grades of acetone oils, vacuum distillation has been employed, making possible closer cuts through the use of fractionating columns, with the resultant saving in steam.

The distillation of creosote oils and wood tars has been stimulated by the great demand for these oils in the flotation industry, and this demand will undoubtedly increase as the flotation process grows in favor. There seems to be a preference for hardwood oils on the part of flotation engineers.

The future of many wood distillers, following the decline in prices of by-products, is problematical, and undoubtedly only those plants equipped for low-cost operation will survive. The smaller plants of, say, under 50 cords daily capacity, will be handicapped when compared with the larger plants and these smaller plants may find it necessary to consolidate to carry on.

The Ferro-Alloy Industry

By **B. D. Saklatwalla**

General Superintendent, Vanadium Corporation of America, Bridgeville, Pa.

Trinity Court Studios

B. D. Saklatwalla

THE FERRO-ALLOY industry has come to the front within the last few years, its importance being recognized during the strenuous times of the World War. Advancement in steel metallurgy has been probably the greatest factor toward the rapid strides of our civilization within the last decade or two, and when we scan the field of improvements in the mechanical, electrical, and transportation industries for the purposes of peace or war, we cannot help but feel that all such strides have been due to the developments of newer and better types of steel, produced by the metallurgist of the present day. While this fact is obviously apparent, it is not generally recognized that these developments have been dependent on the ferro-alloy industry.

The function of ferro-alloys in the manufacture of steel has been twofold. Certain alloys have been used for the purpose of deoxidizing and cleansing, whereas others have been used to impart to the steel certain necessary and desirable physical properties, the alloying element forming an integral constituent of the steel.

The most commonly used ferro-alloys, ferro-silicon and ferro-manganese, function as deoxidizers in the ordinary course of steel-making. They play a double role, however, in the case of high silicon and high manganese steels, where these elements are allowed to remain in the steel in appreciable percentages, in order to obtain certain requisite properties. The electric furnace has practically replaced the blast furnace or the crucible method of production. There also appears to be a tendency to develop mixtures of silicon and manganese [illegible] alloy, whereby several advantages have been [illegible] of these two elements, together with aluminium and titanium, have been recommended for the purpose of deoxidation. The use of such deoxidizers appears to have gained favor in continental Europe, but does not seem to have been taken up in American practice.

As a less commonly used deoxidizer may be mentioned ferro-titanium. This alloy is manufactured in the electric furnace and also by the alumino-thermic process, according as a carbon-containing or a carbon-free alloy is desired. As to the superiority of the one or the other grade there is yet considerable controversy between the different users and makers.

The main metallurgical developments in the manufacture of ferro-alloys within the last couple of years have been in connection with those alloys that form true alloy steels and persist as a constituent of the finished metal. Among such alloys may be mentioned: ferro-chrome, ferro-tungsten, ferro-vanadium, and ferro-molybdenum. The greatest and most recent phase in the development of these alloys is the application of the electric furnace to their production, and the working out of the chemical reactions in the electric furnace, whereby an alloy of suitable purity and carbon content can be directly manufactured from the natural raw ores.

At the beginning of the ferro-alloy industry, the electric furnace was in its infancy, and consequently the field was largely usurped by the alumino-thermic process of reduction. This process has the advantage of convenience and simple equipment, but necessitates the use of more or less pure oxides for reduction, which have to be chemically prepared by an intermediate operation. Such an operation is costly and wasteful, and the aluminium required for reduction is a big item of expense. Recently, however, these deficiencies have been overcome by a very marked development in the art of alumino-thermic reduction. The preparation of pure oxides has been rendered superfluous. Owing to a systematic study of the chemical and thermal nature of the reactions, it has been possible to reduce a complex ore by means of aluminium in conjunction with suitable fluxes, whereby the desired metal or metals are carried into the regulus and the undesirable constituents into the slag. This is accomplished by taking into consideration not only the necessary chemical factors, but also the physical ones, as size of the granules and rate of feeding of the mixture. These factors are technically important when we consider that we are dependent only on the chemical reaction of the mixture for the necessary temperature to obtain a fluid slag and a molten metal, and have no means whatever to control this temperature from any other source. Another marked improvement in the practice of alumino-thermic reduction is the fact that this operation is carried out on a very extensive scale, as a continuous one, in a shaft furnace, tapping the slag and metal at regular intervals. This continuity of operation has not only enlarged the quantity from a few pounds produced in small crucibles to several tons per day out of each shaft furnace, but has helped to produce higher temperatures, owing to large quantities reacting exothermically and storing the heat energy developed in the walls of the furnace, and thus promoting slagging reactions for the undesirable constituents, which was not possible in the small crucibles. This alumino-thermic development has been largely in connection with the production of ferro-vanadium.

The recent developments in the electric furnace for the production of ferro-alloys have been very marked. In the case of ferro-vanadium, for instance, in spite of the great strides of alumino-thermic reduction, the field is now practically dominated by the electric method. The most marked improvements in electric furnace operation have been in the development of a control mechanism, whereby the energy input is held constant by using a true watt regulator. Much higher temperatures have been produced by the use of higher current density, high voltage, and very close electrode spacing. The open-top furnaces have been replaced in several instances by furnaces with closed tops, water-cooled in some cases to conserve the heat energy. The advent of the electric furnace in the ferro-alloy industry has made many low-grade ores available for reduction at a reasonable cost, and thus has not only played a great part as an economic factor in lowering the prices of several ferro-alloys, but also made discarded mineral deposits usefully available, thus increasing our natural resources.

Another direction, in connection with the electric furnace, in which rapid progress has been made, is the refining of ferro-alloys containing undue percentages of carbon and silicon. Activity in this field has been mainly in connection with ferro-chromium. With the development of the so-called "stainless" steels there suddenly appeared a demand for a ferro-chromium very low in carbon content. The amount of chromium present in such steels is high, approximately 12 to 14 per cent, and consequently any appreciable carbon content of the ferro-alloy would cause an undue rise in the carbon of the finished steel. Several patents for refining carbon containing ferro-chromium have been recently granted, and special publicity has been given to some claiming to remove the carbon by bessemerizing the molten alloy with an oxidizing gas. Several processes have also been suggested for oxidizing the carbon content by means of iron ore or chrome ore together with fluxes.

The development of high-chromium, low-carbon steels has also led to processes for introducing the chromium without the necessity of first manufacturing a ferro-chrome. In such processes, the reducing agent, either metallic or nonmetallic, is placed in the bath of molten steel, together with the raw chrome ore, with suitable fluxes, the reduction of the chromium taking place in the molten bath of steel. In this way the reducing agents present in the bath, such as carbon or silicon, are eliminated by oxidation, and the chromium reduced during this reaction enters the steel. This process has the advantage of not introducing carbon with the chromium, and so produces a more homogeneous steel free from segregation, as the chromium reduction takes place uniformly over the entire bath and is absorbed in the nascent state of formation by the steel.

In the ferro-tungsten industry there have been no radically new developments, probably owing to the lack of demand and demoralized condition of the tungsten market.

Another alloy that has gained prominence commercially is ferro-phosphorus. In its manufacture the electric furnace is supplanting the blast-furnace method. Its principal use is to raise the phosphorus content of sheet bars in order to diminish the loss involved in stripping or tearing apart plates or sheets.

Of less importance are the alloys ferro-boron, ferro-zirconium, and ferro-cerium. Ferro-cerium has been used as a pyrophoric alloy and also as a deoxidizer in steel.

In conclusion, it may be mentioned that the United States can claim the furthest advances in the metallurgy of ferro-alloys within the last few years, and to be the largest producer in the world of a commodity on which the progress of our steel metallurgy is so vitally dependent.

Publicity for Chemistry

During the past year the *Yale Alumni Weekly* devoted an issue to chemistry. It was well planned and served to emphasize the part which Yale intends to play in chemistry in the future. Other educational institutions might do well to follow this example.

In *Current Affairs* the Boston Chamber of Commerce has placed before its members an article on the organization of the chemical and dyestuff industry in New England. This cannot fail to bring home to New England manufacturers a realization that the industry is worth keeping and deserves all possible encouragement.

In addition to sending our articles on chemical subjects to papers in nearby towns and cities, the Publicity Committee of the Rochester Section obtained during the last year the equivalent of seventy columns of space in local papers. By assigning each of the local papers to a member of the committee a great deal has been accomplished, and the experience of the committee goes to show that publicity can be obtained for the activities of chemists as an organization and for the accomplishments of individual members, if the material is presented in good form and care is taken to place it in proper hands.

The Michigan Agricultural College Section was the guest at a banquet of the Kiwanis Club in Lansing. The chemists were responsible for the principal addresses, and two hundred and fifty business men were brought into close contact with a large number of chemists. This appeals to us as a good precedent. Such a gathering does more to bring about an *entente cordiale* between chemists and business men than could be accomplished by any number of meetings where one chemist addresses a group of business men or a business man addresses a group of chemists.

Chemical Equipment Manufacturers Petition Congress

Eighty-nine firms, whose names will appear in our next issue and whose business is specifically that of supplying equipment necessary to the American chemical manufacturer and industry, believing that they are in position to have an intimate knowledge of the needs of the chemical industry, have sent the following petition to Congress:

> 1—That the Chemical Manufacturer requires an endless variety and enormous volume of special equipment, the production of which in this country has progressed in step with the developing needs of the Chemical Manufacturer;
>
> 2—That the Chemical Equipment Industry before the War was very small as compared with to day,
>
> 3—That this equipment field represents millions of capital and thousands of employees, both now unemployed to a great extent and, in our judgment, certain to remain so unemployed unless the American chemical industry is properly safeguarded and maintained in a flourishing condition.
>
> 4—Therefore, we respectfully urge that you not only support personally all just provisions for the welfare of our Chemical and coördinate fields, but that you use your good judgment and effort in bringing your colleagues to do likewise, by voting for the Amendment extending the Dye and Chemical Control Act, in accordance with the report and vote of the Finance Committee.

Recent Progress in Magnesium Alloys

By John A. Gann

Dow Chemical Co., Midland, Michigan

MAGNESIUM alloys are now being widely advertised under trade names such as Dowmetal, Magna Metal, M. W. Metal, and Elektronmetal, the last named being a product of the Chemische Fabrik Griesheim-Elektron. All of these alloys are characterized by their high magnesium content, which exceeds 80 per cent and may run as high as 100 per cent. The term "Dowmetal" is a generic one covering an entire series of magnesium alloys, as made by The Dow Chemical Company. Their chemical composition and physical properties vary according to the use for which the alloy is intended. "Elektronmetal" is likewise a generic term. Magna Metal has the same composition as the German Elektron casting alloy. The writer knows very little concerning M. W. Metal beyond the fact that the literature distributed by the M. W. Metal Company is a direct translation of parts of the German Elektron catalog. The commercial production of Elektronmetal dates back to 1912, Dowmetal to 1918, while Magna Metal and M. W. Metal have not yet reached the commercial stage. The Magnesium Corporation of America at Niagara Falls, however, is producing extruded magnesium alloy parts on a quantity production basis.

The published literature relative to magnesium and its alloys is somewhat meager on account of the comparative newness of the subject and the necessity for secrecy on the part of the investigator and manufacturer during the development period and until after they are fully protected. The most recent work on the constitutional diagrams of magnesium alloys is that of Hanson and Gayler[1] which deals with the magnesium-aluminium series. These investigations are quite complete, and confirm in general the earlier finding of Grube. The main difference likely to be of any practical importance is that magnesium is capable of holding about 10 per cent of aluminium in solid solution as contrasted with 6 per cent previously given. The magnesium-rich part of this series has been discussed more in detail by Gann.[2] The relationship between chemical composition, physical properties, microstructure, and equilibrium diagram of these alloys is here shown and some of their industrial applications briefly indicated. Elektronmetal[3] has been described at various times, some of its physical properties given and commercial uses discussed. The most complete report, however, is given in the Elektron catalog, which includes methods of melting, [illegible] of the alloys they are now producing.

The physical properties of magnesium alloys necessarily vary with the chemical composition and method of treatment. Pure cast magnesium, for example, has a tensile strength of only 14,000 to 15,000 lbs. per sq. in. The addition of 6 per cent aluminium practically doubles this value, that is, it increases the tensile strength to 28,000 lbs. per sq. in., while it [illegible] approximately 2 to 3 per cent.

Heat treatment of these alloys results in up to 25 per cent increase in tensile strength, while mechanical working may increase the strength 50 to 100 per cent.

The general characteristics of standard products of the different [illegible] in Table I, the figures being taken [illegible] where necessary, from advertising material. Corresponding values of No. 12 aluminium casting alloy and gray cast iron are given for comparison.

Table I—Comparative Physical Properties of Cast Alloys

Properties	Dowmetal No 1630	Dowmetal No. 217	Elektron Zl	Magna Metal	Aluminium Alloy No. 12	Gray Cast Iron
Tensile strength lb./sq. in.	22,000	28,000	19,000	19,300	20,000	30,000
Yield point lb./sq. in.	14,000	11,000	13,000	6,500	13,000	Indeterminate
Specific tenacity	12,000	16,000	10,400	11,000	7,000	4,200
Per cent elongation (2 in.)	2.0	6.0	2.0	8.5	2.0	Negligible
Brinell hardness	58	50	48	..	70	125
Scleroscope hardness	28	24	13	..	15	30

Table II—Physical Properties of Dowmetal Alloys

	Dowmetal No. 220	Dowmetal No. 1045	Dowmetal No. 1630	Aluminium[1] Alloy No. 12
Tensile strength lb./sq. in.	22,000	22,000	22,000	20,000
Yield point lb./sq. in.	14,000	14,000	14,000	13,000
Per cent elongation (2 in.)	2.0	2.0	2.0	2.0
Brinell hardness	58	58	58	75
Scleroscope hardness	28	28	28	15
Single blow impact[2]	26	32	40	26
Impact fatigue blows[3]	1,300	2,800	3,200	200
Maximum fiber stress, lb./sq. in.[4]				
200,000 reversals	6,000	8,900	11,000	
40,000,000 reversals		8,050	9,800	

[1] Sand cast in our own foundry.
[2] Dow machine.
[3] Eden-Foster machine.
[4] Farmer alternating stress machine.

Probably the most recent advance in magnesium alloys is the production of new Dowmetal piston alloys, in which the toughness and fatigue endurance have been very materially increased without any sacrifice whatsoever in other desirable properties. An exhaustive study of this subject is now in progress, and although this program is still in the elementary stages the results are of interest (see Table II). Our results on No. 12 aluminium alloy are again given for comparison.

Within the last two months a new alloy especially designed for use in high-speed motors and in racing cars has been developed. This alloy has a thermal conductivity nearly 70 per cent higher than the usual magnesium-rich alloy, thereby insuring a cooler running motor, while the toughness and impact fatigue endurance are fully as high as that of the alloys listed in Table II. The excellent results obtained in actual service from these various Dowmetal pistons indicate great possibilities in the future development and use of magnesium alloys.

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[1] [illegible]

[2] [illegible]

[3] [illegible] 40 [illegible] 316 [illegible]

The Second Annual Report of the Scientific and Industrial Research Council of Alberta, covering work done during the year 1921, has just been printed. The greater part of the work was done in relation to various types of fuels, although considerable attention was given to road materials, forest products, and a geological reconnaissance in Alberta.

Nonferrous Alloy Progress in 1921

By **H. W. Gillett**

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THE YEAR 1921 was one of business depression in which the nonferrous metal industry was hard hit. Prices of nonferrous metals were low, and production and consumption were at a minimum. Such conditions do not make for rapid commercial progress. In the general retrenchment, research laboratories in this field had to let many workers go, so that the scientific output fell off somewhat in quantity, though not in quality.

Light Aluminium Alloys

The light aluminium alloys received much attention. Cast alloys of the general type of 85 Al: 15 Si began to be tried out commercially, one automobile firm trying out one hundred crank-cases for an 8-cylinder car, and smaller castings of this alloy being used by various firms. This alloy bids fair to rival and perhaps to supplant the long-established No. 12 alloy of 92 Al: 8 Cu, as it has a lower specific gravity, a higher tensile strength, and a decidedly greater ductility. In the foundry it appears to behave as well as No. 12, though it requires some variation of foundry practice. If service tests bear out the improved physical properties shown by laboratory tests, we may expect quantity production and use of the new alloy to follow slowly.

In that case, the interesting problem will arise of the direct production of Al-Si alloys from lower grade ores, possibly from clay. At least some simplification of the process of purification of bauxite might become possible, perhaps resulting in a lowering of the cost of production of this alloy and its more extended use. Wrought alloys of the Duralumin type (*e. g.*, 96.5 Al, 3 Cu, 0.5 Mg) have been the subject of a good deal of work which has been timely because of the tragedy of the ZR2, which was ascribed to failure of Duralumin. Merica and his co-workers at the Bureau of Standards published several papers dealing with Duralumin.

Jeffries and Archer, in an epoch-making discussion of the theory of hardening by slip-interference, considered the mechanism of the hardening of Duralumin as previously suggested in less detail by Merica, tied it in with the mechanism of the hardening of steel, and gave the metallurgical world a well-rounded theory, which, in conjunction with X-ray crystal analysis, gives us a basis for a more plausible answer to the riddle of "What is martensite in steel?" than we have had before, as well as showing the basic requirements that the equilibrium diagram of any alloy must meet in order that the alloy may respond to heat treatment.

Merica and Jeffries and Archer ascribed the hardening of Duralumin to the precipitation of the compound $CuAl_2$. British investigators at the National Physical Laboratory, however, produce strong evidence that the hardening agent is another compound, Mg_2Si. It appears that both compounds play a role but that of the Mg_2Si is predominant. If this is true, the discovery and development of Duralumin has been due to the fact that the commercial aluminium has in the past contained as an impurity the 0.25 to 0.35 per cent Si that is required to form Mg_2Si in sufficient quantity to give a properly hardening Duralumin. The Aluminum Company of America has recently produced small amounts of aluminium of extreme purity and is working on the question of the hardening agents in Duralumin and of the effect of silicon. The purity of the aluminium available will allow them to carry the study to lower silicon contents than has hitherto been possible.

The National Physical Laboratory of England has brought out a modified Duralumin which they designate as "Y" alloy, which contains a little more Cu than the usual Duralumin and 2 per cent Ni also, the aluminium content being correspondingly decreased. This alloy is claimed to be the equal of Duralumin on all usual tests and to surpass it in resistance to repeated stress at 150° C. It is described in detail in the Eleventh Report of the (British) Alloys Research Committee, which covers also a good deal of work on ternary aluminium alloys of the type containing about 3 per cent Cu and 20 to 25 per cent Zn, with or without a little Mg and Mn in the wrong condition. These alloys, in castings, give the highest ratio of tensile strength to density of known cast aluminium alloys.

Rolling these alloys was a task requiring much patience but with suitable precautions it can be done, and material of 90,000 lbs. tensile strength per sq. in. can be produced. Another British investigation of interest was that of Carpenter and Elam on "Recrystallization of Aluminium Sheet."

Besides the work of Jeffries and Archer on the theory of hardening, they have discussed the question of grain size (a problem that has also received attention from a number of British investigators). Other contributions from the research staff of the Aluminum Company of America have dealt with the density of molten aluminium and Al-Cu alloys at various temperatures, and with the heat treatment of castings.

Anderson, of the Bureau of Mines, has continued his work on practical problems relating to the preparation of aluminium alloys, dealing with cracking of castings in the foundry-gas atmospheres in aluminium-melting furnaces, iron-pot furnace practice, etc.

The use of aluminium alloy pistons in automobile engines appears to be progressing slowly. Some cars that previously used them have gone back to cast iron, while other cars have started to use them. As a result of improved design, recent aluminium pistons appear to be giving better results than earlier ones. Magnesium alloy pistons are being tried out, but the situation on Dowmetal, electron alloy, and similar alloys of a magnesium base seems to be one of general interest but little actual use as yet.

Heavy Aluminium Alloys

Of heavy alloys into which aluminium enters, aluminium bronze is the most important. Blue discussed the heat treatment of this alloy and pointed out that he had found the alloy unreliable because of the uncertainty of getting the same results twice and the difficulty in commercial production of getting the physical properties claimed for it on the basis of laboratory tests. This drew emphatic replies from producers of the alloy, but Blue countered by showing that his arguments were based on tests of alloys produced and heat-treated by his critics themselves. A translation from the French of Grard's book on aluminium and its alloys has been published, which deals with the heat treatment of aluminium bronze, as well as exhaustively discussing aluminium and its light alloys.

BRASS AND BRONZE

Some attention has been paid, especially by French workers, to heat treatment of brasses and bronzes.

The research department of the Woolwich (England) Arsenal has published in the *Journal of the British Institute of Metals* three important papers, one by Genders on "The Extrusion Defect," which, with its discussion, covers many interesting points of the general subject of extrusion of metals, and one by the same author on "Casting Brass Ingots." The other, by Moore and co-workers on "Season Cracking of Brass," is extensive and has aroused much comment.

Corrosion of brass and Muntz metal has been dealt with by Rawdon of the Bureau of Standards. British investigators continued work on corrosion of condenser tubes. Another British investigation of scientific interest is that of Haughton on the copper-tin equilibrium diagram.

The American Brass Company has given a very fine paper on "Grain Growth in Alpha Brass." This firm has also made noteworthy application of spectroscopic analysis to routine laboratory work. The Scovill Manufacturing Company presented in THIS JOURNAL a method for electrolytic determination of very small amounts of lead.

The General Electric Company put out its new bearing metal, "Genelite," made by mixing oxides of copper, tin, etc., with an excess of graphite, reducing and compressing, giving an alloy carrying graphite mixed all through the material and hence having self-lubricating properties. The material is probably not applicable to a very wide field, but will fit in well for some uses.

The Anaconda Copper Mining Company, producers of copper and zinc, has taken over the American Brass Company, the largest producer of brass.

The competition of aluminium and nickel alloys, more recently rolled and extruded zinc, and still more recently of the new stainless iron (low carbon steel with around 15 per cent chromium) has threatened to cut into the fields heretofore served primarily by copper, brass, and bronze. The producers of copper and its alloys have therefore formed the Copper and Brass Research Association, whose function is to combat this encroachment and to develop new fields for the copper alloys. The organization does not cover the field that its name implies to a chemist or metallurgist, as it deals so far only with commercial research," *i. e.*, propaganda and advertising (on a sane and reasonable basis), and not with chemical, physical, and metallurgical research. The field proposed by the National Research Council, which was to be covered by the Alloys Research Association but which materialized only in a limited information service on alloys, is still unfilled. The British Nonferrous Metals Research Association, with headquarters in Birmingham, appears to be getting a good start.

Notwithstanding the depression of 1921, the various brass rolling mills which had previously laid down plans for extensive installations of electric furnaces, went ahead with the installations, which is pretty good proof that electric brass melting is expected to continue to show lower melting costs than fuel-fired furnaces in the more normal times ahead, as well as under the conditions during and just after the war. Electric melting of brass and bronze has had a very rapid growth. There are to-day more electric brass furnaces installed in the United States than electric steel furnaces. While the average brass furnace is smaller than the average electric steel furnace, the percentage of electrically melted brass, in comparison with the total annual output, is greater than that of electrically melted steel.

NICKEL

Pure nickel and such alloys as Monel metal continue to find increasing application. Madsen has described before the American Electrochemical Society notable advances in the production of ductile electrolytic nickel, and Merica, of the International Nickel Company, has published a collection of data on the properties of nickel and its alloys.

Guillet, the French metallurgist, has discussed in *Chemical and Metallurgical Engineering* the replacing powers of various elements for zinc in brass. An alloy of about 46 Cu: 10 Ni: 44 Zn is of particular promise.

Foundrymen in this country were forced to use up a good deal of cupro nickel, shell-band scrap containing a little nickel, in recent years, and much of this went into alloys as if it were pure copper, giving alloys with small amounts of nickel. The generally satisfactory results have raised the question whether intentional additions of nickel may not be quite generally useful in copper alloys, since it forms a solid solution with copper that is stronger than copper, just as it forms a solid solution with iron and strengthens the ferrite, so that one may increase the strength of almost any steel by addition of suitable amounts of nickel.

The producers of nickel are naturally interested in this, and developments on this line may be looked for in the future.

COBALT

One interesting development in connection with the cobalt-chromium cutting alloy, stellite, is that the producers are making commercial inspection of stellite tools by the X-rays, to detect blowholes and other defects in the cast tools. The application of X-ray examination to metals is being carried farther than in the past and still further improvements are expected to be attained in the near future.

ZINC

Marked advances have been made in the application of rolled and extruded zinc to industrial use. Its cheapness and resistance to atmospheric corrosion make it useful for a multitude of uses. A paper by Mathewson of Yale and co-workers of the New Jersey Zinc Company in the *Transactions of the American Institute of Mining and Metallurgical Engineers* gives great detail on the properties and applicability of the material. One by Ingall in the *Transactions of the British Institute of Metals* on "Mechanical Properties and Microstructure of Rolled Zinc" supplements the American paper.

GENERAL

Steady progress is being made in fields that touch the interests of the chemist and metallurgist working on nonferrous alloys. Refinements and more speedy methods in chemical analysis, improvements in methods of physical testing, more knowledge of endurance testing, advances in metallography, etching practice, and photomicroscopy apply to the nonferrous as well as to the ferrous field.

Theoretical problems in atomic and crystal structure and arrangement, the study of space lattices by the X-ray spectrometer, grain growth and recrystallization, the study of colloids and the application of colloid chemistry to metals and alloys bear on both ferrous and nonferrous alloys, and to discuss them here would take us outside the scope of this review.

It is interesting to note that some of the advocates of the "amorphous cement" theory appear to be modifying their views somewhat, especially in regard to cast metals, and opposition to the theory is beginning to be expressed as vigorously as is its propagation and defense. This will incite the collection of more experimental facts and more rigorous examination of the explanations for them, so that ultimately we shall know a good deal more of the truth.

Meanwhile, the arguments pro and con will continue to make the discussions of metallurgical papers lively.

Conclusion

The above represents the personal "reaction" of the reviewer on the more important features of nonferrous alloy progress in 1921. Another reviewer might pass over most of these and cite many other developments, commercial and scientific. The interested reader will find the detailed nonferrous history of 1921 in the following (rated in classes according to usefulness to the writer).

Class 1—*Transactions of the American Institute of Mining and Metallurgical Engineers*; *Journal of the Institute of Metals* (abstracts valuable as well as papers. Most of the abstracts available in *Chemical Abstracts* but more readily used in *J. Inst. Metals* on account of being collected and classified); *Chemical and Metallurgical Engineering*.

Class 2—*The Foundry*; *The Iron Age* (contains many nonferrous data); *Metal Industry (N. Y.)*; *Metal Industry (London)*.

Class 3—*Revue Metallurgie*; *Zeitschrift fur Metallkunde*; *Engineering (London)*.

Class 4—*Brass World*; *Metall und Erz*.

Physical Chemistry as Applied to Foods

By **Carl L. Alsberg**

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THE SLOP JAR used to be the destination of most of the colloidal substances the chemical investigator encountered. What did not crystallize he stigmatized as a smear. Yet what does not occur in nature in the crystalline form is at least as important to man as what crystallizes, for it constitutes the essential portion of organized beings. Until well toward the end of the last century only the biochemist or the physiologist concerned himself with such material. It was necessary for the biochemist to pioneer in this field and for the science of physical chemistry to have developed before the study of such colloidal, not readily crystallizable material became interesting to chemical investigators generally. Solely by means of the application of the principles of physical chemistry to the study of the colloidal materials that characterize living organisms has progress in many branches of biological science become possible. Such phenomena as the acid-base equilibrium in animals and plants, the maintenance of neutrality, the transport of carbonic acid through the blood, the mechanism of secretion and excretion, cell respiration, the osmotic phenomena exhibited by living semi-permeable membranes, and the metabolism of microörganisms came to be understood only when conceptions of physical chemistry began to be applied by the biochemist in the study of biochemical phenomena. Studies upon the true character of acidity and alkalinity, upon dissociation, the phase rule, emulsions, sols and gels were necessary before some of the apparently simpler problems of biology could be studied. It is fair to say that to-day the science of general physiology is based very largely upon the science of physical chemistry. Each advance in physical chemistry is liable to be followed by a corresponding broadening of our knowledge of the behavior of living things. It is obvious that only through such knowledge can progress be made in many branches of medicine. Thus, to physical chemistry must be attributed much of what we know about the coma that may result from the disturbance of the acid-base equilibrium in the body, which the pathologist knows as acidosis, so common a cause of death, especially in diabetes.

Since agriculture and food manufacture are essentially forms of applied biochemistry, physical chemistry has made possible great advances of immediate practical usefulness. Without physical chemistry our present-day conceptions of the equilibria that prevail in soils and in the soil solution would be impossible. An increase in our knowledge of the behavior of colloids and of emulsions is destined to influence profoundly the world's methods of food production. For example, wheat owes its preëminence as a bread grain in large measure to the fact that it contains a mixture of proteins known as gluten, which, when mixed with water, forms a tenacious, elastic mass. For this reason wheat and, to a less degree, rye alone of all the grains yield dough. Because of the physical qualities of gluten—its toughness, its distensibility, and its coagulability by heat—it is possible to produce leavened bread. These qualities of gluten—elasticity and coagulability—however, are physicochemical, not purely chemical qualities in the ordinary sense. They do not depend primarily upon the arrangement of the atoms in the molecule but rather upon the physical condition of molecular aggregates. If, then, the properties of gluten which render wheat so desirable as a bread grain are physicochemical, they depend upon the physicochemical condition of the protein molecule, not upon its chemical structure. It is not too much to hope that physicochemical research upon colloids will one day enable us to control the colloidal state to such an extent that we can give to a colloid essentially those physicochemical properties that we desire. If this can be done, and there is no inherent impossibility in the idea, it may be possible to give to other proteins besides gluten the physicochemical properties of gluten. When that time comes, leavened bread will be produced from materials or grains other than wheat and rye. What this would mean to the food supply and the future of the race is obvious. Indeed, before such profound developments take place, it is probable that the application of physical chemistry to the food industries will render them vastly more efficient. To-day the milling and baking chemists are studying the hydrogen-ion concentration of milling and baking materials and are coming to realize that this is one of the most important, if not the most important, factor in determining the bread-producing qualities of flours and the behavior of doughs in fermentation. It is not improbable that in the milling laboratories of the country the potentiometer before long will be as familiar an instrument as the buret. What is likely to be true in the mill is likely to be true in the bakery, in the creamery, and in the sugar refinery. The behavior of dough and yeast is profoundly influenced by physicochemical conditions. Butter is an emulsion. The colloids of cane and beet juice play an important part in molasses formation, while the problem of decolorizing carbon is one for the physical chemist. Examples might be multiplied vastly, were space available. It is perhaps sufficient to add, in conclusion, that most of the industries that elaborate raw materials derived from living beings have to deal with colloids. Therefore they can make progress only so fast as they apply to their problems the discoveries made in that branch of physical chemistry which is known as colloid chemistry.

An Outline of the History of Chemistry Symbolically Represented in a Rookwood Fountain

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THERE are certain symbols and figures that are typically characteristic of the foremost periods in the History of Chemistry. The reproduction of some of these symbols and figures and their artistic embodiment in a fountain[1] of Rookwood faience has been accomplished in a remarkably unique and harmonious style by the master artists and ceramic craftsmen of the Rookwood Pottery of Cincinnati.

An appreciation of the symbolism of this fountain from the twofold point of view of the *history* and the *motive* of chemistry calls for a brief outline of the motives of the foremost periods in the history of chemistry accompanied by a description of the principal symbols and figures that have marked these periods. The five generally recognized overlapping periods, the predominant ideas in any one being accepted far into another, are approximately as follows:

1—*The Prehistoric Period*, from prehistoric times till 1500 B. C.
2—*The Alchemical Period*, from 1500 B. C. till 1650 A. D.
3—*The Iatrochemical Period*, from 1500 A. D. till 1700 A. D.
4—*The Phlogiston Period*, from 1650 A. D. till 1775 A. D.
5—*The Quantitative Period*, from 1775 A. D. till 1900 A. D.

The science of chemistry is defined by J. B. Mellor[2] as "man's attempt to classify his knowledge of all the different kinds of matter in the universe; of the ultimate constitution of matter; and of phenomena which occur when the different kinds of matter react one with another." Since all material transformations, physical or chemical, are accompanied by energy transformations, it follows that the extent of our knowledge of these changes and the ultimate constitution of matter determines the subserviency to mankind of both matter and energy. Accordingly, the motive of the science of chemistry as well as that of other natural sciences has been expressed in a broad and comprehensive sense by a maxim of Galileo Galilei (1564–1642) which is the motto of the fountain: "Let us remember, please, that the search for the constitution of the world is one of the greatest and noblest problems presented by nature." This applies not only to man's search for the ultimate constitution of the atom from the time of the Hindu philosopher, Kanada, 1200 B. C., to the researches of J. J. Thomson, Bohr, Rutherford, and Langmuir, but also to the past and present quests for the limits of the universe which according to the metaphysics of relativity and Einstein may be finite.

Berthelot, in his work, "*Les Origines de l' Alchemie*,"[3] writes:

> Chemistry is not a primitive science, like geometry and astronomy; it is constructed from the debris of a previous scientific [illegible] [illegible]nerical and half positive, itself founded on [illegible] amassed by the practical discoveries of metallurgy, medicine, industry, and domestic economy. It has had to do with alchemy, which pretended to enrich its adepts by teaching them to manufacture gold and silver, to shield them from diseases by the preparation of the panacea, and finally [illegible] them with the soul of the world and the universal spirit.

Egyptian hieroglyphics and picture writings show that many of these practical discoveries were the fruits of Egyptian Alchemy, but the Chaldeans were in fact the pioneers of alchemical science. Although no written record of Chaldean Alchemy has been discovered, we are aware that the number "7" was greatly respected in their philosophy and religion. They recognized seven visible planets, seven gods of heaven, seven gods of earth, and seven devils. The Chaldean philosophy also connected the properties of the seven metals with the influence of the seven planets and both in turn with the functions of the organs of the human body and the destinies of men. Now since these ideas originated in the Prehistoric Period and were maintained throughout the subsequent periods (and are even given credence by some to-day), it is appropriate that the seven Chaldean symbols, which represent simultaneously the seven planets and the seven metals, be embodied in the crowning arch of the fountain. Thus from left to right (Fig. 1) across the top are noted the symbols for the Sun or gold, Venus or copper, Mars or iron, Jupiter or tin, Saturn or lead, the Moon or silver, and Mercury or mercury.

The second and longest period in the history of chemistry, that of Alchemy, extends through thirty centuries—from 1500 B. C. to 1650 A. D. A series of books attributed to Hermes Trismegistus, a native of Babylonia, whom the Egyptians regarded as a god of wisdom, and other ancient records clearly indicate the existence of purely empirical technical arts such as glass-making, pottery, dyeing, painting, tanning, brewing, baking, the preparation of poisons and their antidotes, antiseptics and oils, expressed and distilled. While these are branches of alchemical knowledge, the word "alchemy" is more especially used to designate the manufacture, or better said, the sophistication of silver and gold.

With the development of various technical processes and the effort to transmute the metals, there was associated a great philosophical folly, namely, the search for the philosopher's stone and the elixir of life. Before considering the doctrine of transmutation, the philosopher's stone and related symbolism, it is consequential to note some contributions of the Greek philosophers to alchemical thought. They were not chemists. Few observations or experiments were made because they preferred to argue from general principles to particulars rather than from particular observations to general principles. Nevertheless, they clearly enunciated without any experimental foundation whatever the fundamental principle of all sciences—the law of the conservation of mass—and portrayed qualitatively the atomic constitution of matter.

Empedocles of Agrigentum (490–430 B. C.) divided all matter into four elements—fire, air, water, and earth—which were retained in the natural philosophy of Plato (427–347 B. C.) and of Aristotle (384–322 B. C.). It was due to the intellectual prestige of Aristotle that his idea of the transmutation of the four elements became the dominant motive of the period of alchemy. Fire, air, water, and earth were the roots of all things, endowed with the property of being without beginning, indestructible and homogeneous. From the mixtures of these four elements, which carried, respectively, the principal qualities, heat, cold, wetness, and dryness, arose all substances as we perceive them. The properties of substances were attributed to the fundamental properties of the elements of which they were composed. Hence, elements were transmutable one into the other by the abstraction of certain qualities and the substitution of others.

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[1] [illegible] 1921 [illegible]

[2] [illegible] 1922

[3] [illegible]

The transmission of Greek philosophy to the peoples of the west was the result of the conquest of Spain (711 A. D.) by the Arabs, who contributed enormously to the increase of chemical knowledge. Geber,[4] the 8th century Arabian chemist, developed the Aristotelian conception of the constitution of matter so as to account for the observed differences between the seven metals and to supply a theoretical basis for their transmutation. The four elements of Aristotle were retained as the ultimate constituents but the substances *mercury* and *sulfur* were assumed as the more proximate ones; mercury being the vehicle of the qualities of ducility, fusibility, and luster; and sulfur the bearer of the property of combustibility. Accordingly, the change of one metal into another should consist in the addition or withdrawal of one of the two constituents, sulfur and mercury, or in its purification.

Geber's Two-Principle doctrine held sway for seven centuries. Basil Valentine (second half of the 15th century) added a third principle or element, *salt*, representative of that which is permanent and unaltered by the action of heat. This Three-Principle doctrine became dominant for two centuries. It was accepted entirely by Paracelsus (1493–1540?) who made alchemy the servant of medicine.

The great work of Paracelsus was in effecting a breach with tradition and setting physicians and alchemists free from the bondage in which they were held by convention. He borrowed his medical treatments from barber-surgeons, old women and quacks, and employed powerful and dangerous medicines prepared from mercury, opium, and antimony more boldly and successfully than his predecessors. Paracelsus taught that the object of chemistry was not to make gold but to ameliorate disease. The art of making drugs, the motive of the Iatrochemical Period, thus became one of the original branches of alchemy, but it was frequently obscured by combined searches for the philospher's stone and the elixir of life.

Paracelsus also promulgated the Three-Principle doctrine so vigorously that it became associated with his name. It is a question whether these three principles—sulfur, mercury, and salt—were accepted by chemists instead of the four Aristotelian elements or alongside with these. Since "elaborate ambiguity, direct contradiction and studied vagueness are the characteristics of alchemical style," it would be useless to attempt to prove anything by directly quoting alchemical manuscripts. Nevertheless, the following excerpt from "A New Light of Alchymia," 1607, by Michael Svandivogius, is typical of medieval speculation relative to the interrelationships of the four elements (Aristotelian), fire, air, water, and earth, and the three principles (Paracelsian), sulfur, mercury, and salt. (Note arrangement of symbols in Fig. 1.)

> We will now descend unto the Principles of things. . . . But how they are produced of the foure elements, take it thus. . . . The Fire began to act upon the Aire, and produced Sulphur, the Aire also began to act upon the Water, and brought forth Mercury, the Water also began to act upon the Earth and brought forth Salt. But the Earth since it had nothing to work upon, brought forth nothing, but that which was brought forth continued and abided in it. Wherefore there became only three Principles, and the Earth was made the Nurse and Mother of the rest. . . .These three Principles are altogether necessary because they are the near matter . . . The remote are the foure elements out of which God alone is able to create things. . . . By the due separation, and conjunction of these Nature produceth as well Metalls, as Stones in the Minerall kingdome; but in the Vegetable Kingdome Trees, Herbs, and all such things; also in the Animal Kingdome the Body, Spirit, and Soule, which especially doth resemble the work of the Philosophers. The Body is Earth, the Spirit is Water, and Soule is Fire, or the Sulphur of Gold.

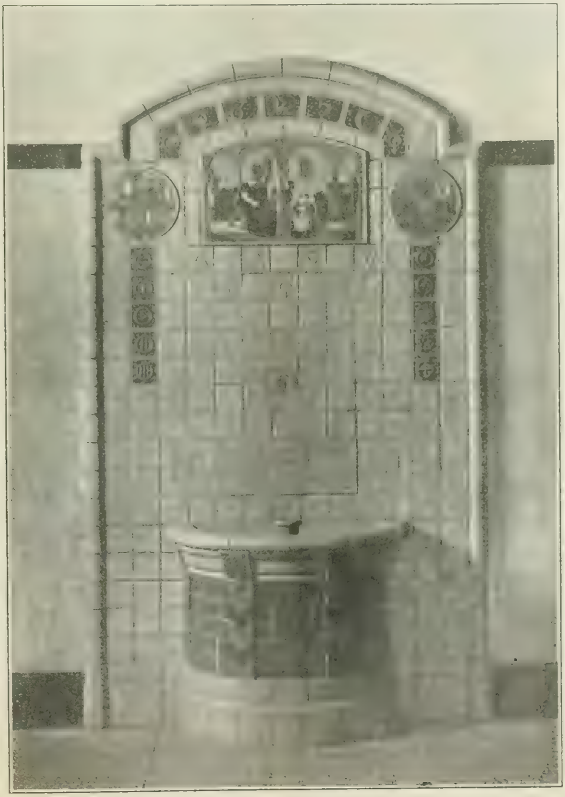

FIG. 1—THE FOUR TRIANGULAR SYMBOLS FROM LEFT TO RIGHT REPRESENT THE *Four Elements:* FIRE, AIR, WATER, AND EARTH. THE THREE UNDERLYING SYMBOLS REPRESENT THE *Three Principles:* SULFUR, MERCURY, AND SALT. THE SYMBOL FOR *Phlogiston* IS BELOW THAT OF MERCURY. DIMENSIONS: 5′ 2″ x 8′ 4″

Thus was alchemy in the 16th century complicated by religious ideas. It was even argued that the exact and natural sciences proceed by induction and deduction while the occult and spiritual sciences proceed by analogy. Following out this line of thought the alchemists produced the following remarkable triology:

MATERIAL WORLD
Sulfur
Mercury
Salt

HUMAN WORLD
Body
Soul
Spirit

DIVINE WORLD
Father
Son
Holy Ghost

Each of these was a trinity in unity, and a unity in trinity. In each world was a distinct design: in the material, the perfection and the metals; in the human, the perfection of the soul; in the divine, the contemplation of the Deity in His splendor.

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[4] Freund's "Study of Chemical Composition," Cambridge University Press, **1904**, and J. Campbell Brown's "History of Chemistry," Churchill, London, **1913**, are chief sources in following descriptions.

The mystic alchemists interpreted the Three Principles in their own fashion. Mercury, the passive and female principle, was *matter;* sulfur, the active and male principle was *force* or *energy;* and salt, the middle term in the proposition, was *movement*, which applied force to matter. In other terms, mercury was the *subject;* sulfur, the *cause;* and salt, the *effect*. Such, in brief, was the involved philosophy of the alchemists.

Symbolism highly typical of the achemical transmutation doctrine and the philosopher's stone motive is found in the circular plaques in the upper left- and right-hand sections of the fountain (Fig. 1). The one to the left is a reproduction of a drawing taken from Kelly's medieval work, *Theatre of Terrestial Astronomy*. Its subject, the *Mutual Conversion of the Elements*, represents a black rock, on the top of which stand the variously colored figures of Saturn, Jupiter, Mars, Sol, Venus, Mercury, and Luna. On the black plain in the foreground are Mercury and Luna, labeled *Hermaphrodita*, with a crescent on her head. To the left of Mercury and to the right of Luna close observation detects the symbols of mercury and sulfur, respectively. The four elements blow from the four corners upon the place where Mercury stands with Luna. This plaque illustrates how the latter alchemists, who were astrologers as well, laid special stress, as did the earlier Chaldean alchemists, upon the influences of the seven heavenly bodies, each producing the metal it typified. Paracelsus even pretended to be able to calculate when and how this planetary influence took effect.

A description of the doctrine of transmutation would not be complete without some account of the philosopher's stone, which was "the universal medicine for giving perfection," the constant aim of the alchemists. They treated the symptoms of the metals as the doctor treats those of a sick man when he does not know the cause of his patient's illness. They tried to remove the symptoms of illness and induce those of health or perfection. As the centuries passed,

> the alchemists became more and more extravagant in their visions, and attributed unlimited powers to the philospher's stone, such as making precious stones, curing diseases, prolonging life, and controlling elemental spirits. It could preserve health, raise the dead, make the old young, turn the coward into a hero, strengthen the memory, and sober the drunkard! [BROWN]

The circular plaque of the upper right-hand corner of the fountain (Fig. 1) is a copy of *The Birth of the Philosopher's Stone* from *Der Hermetische Triumph*, Amsterdam, 1689. The alchemists assumed that the material of the stone or elixir embodied: 4 angles in its virtues: fire, air, water, and earth; 3 angles in its substance: sulfur, mercury, and salt; 2 angles in its matter: the fixed and the volatile; 1 angle in its radical principle: the *prima materia*. The sum of these angles is 10, which number in their Cabala, or mystic system, was held to express the material of the philosopher's stone. A close inspection of the heterogeneous details of the plaque reveals most of the angles just noted. There are fire, air, water, and earth. The symbol of sulfur is immediately above that of mercury which consists of intertwined serpents. The hermetically sealed flask beneath, or the philosopher's egg, in which prolonged heating operations were conducted, is above fire. The sun and the moon, *i. e.*, gold and silver, direct their rays or influence into the egg. The opinion prevailed that the philosopher's stone must be produced by the union of metals, and *a fortiori* of the perfect metals

This survey of the alchemical period may be fittingly concluded by directly quoting the estimate of J. Campbell Brown:

> When we reflect upon . . . the philosophy and aims of the alchemists, we perceive how foolish it would be to sum them up in a single epithet. The men belonged to distinct classes. There were mystical or religious alchemists who made use of terms of art merely as parables, and alchemical processes as allegories. Their real subject was the human soul; their true object the guidance of mankind to salvation. But these were few. There were philosophical alchemists, steeped in the doctrines of Aristotle, who sought by the transmutation of base metals into gold to prove their great thesis—the unity of all things. There were scientific alchemists, whose desire was to discover the properties and combinations of metals, and the best methods for their manipulation. And there were mercenary alchemists, who hoped to find in the philosopher's stone the key to a store of unlimited riches. Unless we keep these different classes in mind, and differentiate clearly between them, we shall never understand all that is implied in the title 'alchemist.'

The mystic symbolism of these circular plaques is offset by the larger, central double-panel reproduction of a Medieval Soda Plant. The original illustration appears in the *De Re Metallica* of Georg Agricola, who records the following self-explanatory description:

> The solution from which soda (natron or hydrous sodium carbonate) is obtained is made of sweet water percolated through earth that is full of soda or lye from the same being percolated through oak ashes. Each solution is caught in tubs and poured into quadrangular copper caldrons and boiled till it condenses to soda. Then it is poured out into casks which contain copper wires, to which the soda adheres and hardens and becomes copper-green, or what we call borax, to use a Moorish name. Pliny tells us that formerly soda was mixed with copper rust and rubbed with copper in copper mortars.

The third and fourth or the Iatrochemical and Phlogiston Periods in the History of Chemistry are practically synchronous, extending from the beginning of the 16th to nearly the 19th century. The Iatrochemical Period is marked by the motive to produce and investigate medicinal substances by chemical means, and the production of chemical compounds in the search for new medicines, rather than the alchemical search for the philospher's stone which was not, however, entirely abandoned. The philosopher's stone motive became the *elixir vitae* motive. The symbolism described is typical both of the Alchemical and Iatrochemical Periods.

The Phlogiston Period is marked by a more sincere and precise search for chemical truth, and especially by the rise, development and fall of a remarkable theory of combustion which brought together as related processes a number of diverse phenomena that at first appeared to have nothing in common, namely, combustion, acidification, respiration, reduction, and the solution of metals in acids. All combustible substances were assumed by G. E. Stahl (1660–1734), the founder of the phlogiston theory, to consist of the product of combustion plus a hypothetical, inflammable substance termed "phlogiston," which corresponded to the fire matter of the ancients or to sulfur of the alchemists. Substances in burning lost the phlogiston. Lavoisier later demonstrated *quantitatively* that combustion was due, not to the loss of phlogiston, but to a direct combination of the combustible substance with the oxygen of the air, and thus at one blow overthrew the phlogiston theory and established the oxygen theory of combustion.

The symbol for *phlogiston* is near the center of the fountain, below the symbols for the four elements and the three principles (Fig. 1) and above Lavoisier's famous apparatus in which the synthesis and analysis of mercuric oxide were demonstrated.

The ideas of the constitution of the philosopher's stone were conflicting, and the opinions of the alchemists as to the number of operations involved in its synthesis are various, but the process was made to imitate the operations of Nature and accordingly was prolonged through seven stages, each corresponding to the influence and invocation of one of the seven planets. Thus for each planet, the philosopher's egg was heated a fixed number of days, the total operation occupying no less than 217 days, or over seven months. The perfected philosopher's stone was reputed to be a red powder which, when projected upon a quantity of molten base metal in a crucible, would transform it into an ingot of pure gold.

A word of appreciation is due the phlogiston theory for the great service it rendered in effecting the correlation of diverse phenomena and promoting the development of chemistry along scientific lines. While the phlogiston theory was radically wrong, we must realize, as Whewell states, that "If our hypothesis renders a reason for the agreement of cases really similar, we may afterwards find the reason to be false, but we shall be able to translate it into the language of truth."

It was Anton Laurent Lavoisier (1743–1794) who effected this translation. His advent and achievements mark the establishment of chemistry as a science, to which he contributed more than any previous investigator through quantitative methods of procedure. Lavoisier's theories and works initiate the fifth, or the Quantitative Period, in the history of chemistry. Using the apparatus noted in the small panel at the center of the fountain—a retort, resting on a charcoal furnace, with a curved neck communicating with a bell jar—Lavoisier effected the quantitative synthesis and analysis of mercuric oxide. This work not only established the oxygen theory of combustion but demonstrated quantitatively for the first time the principle of the conservation of mass.

In relation to Lavoisier, also note the four tiles in the circular rim of the drinking basin of the fountain, which illustrate a special glass vessel of alchemical origin termed a "pelican" and used for prolonged heating operations involving the circulation and condensation of vapors. In such a vessel, formerly used as the philosopher's egg in which alchemists endeavored to generate the philosopher's stone, Lavoisier boiled a given weight of pure water for 100 days and demonstrated that the earth which appeared in this water was from the disintegration of the previously carefully weighed vessel, and not due, as was generally believed, to the transmutation of water into earth. This, of course, undermined transmutation ideas. He further proved that water was not an element, but a compound of hydrogen and oxygen, and defined an element as a substance which we have *not as yet* been able to resolve into other substances.

Brief note must now be made of the concomitant rebellion against the Aristotelian and transmutation doctrines which held sway throughout the Alchemical, Iatrochemical, and Phlogiston Periods. Pronounced instances of this rebellion became common toward the end of the 17th century and are especially noted in the works of Van Helmont, Francis Bacon, René Descartes, Pierre Gassendie, Robert Boyle, and Isaac Newton, most of which tended strongly toward the reëstablishment of the conceptions of the Greek atomistic philosophers, Democritus, Epicurus, and Leucippus. These ancient writers held a view of the constitution of matter which in most astonishing respects agrees with many of our modern views. But the fundamental distinction between the ancient and the modern doctrines lies in the fact that John Dalton (1766–1844) transformed mere *qualitative speculations* into a *practical quantitative theory* by assuming that chemical combination occurs between simple numbers of elementary atoms of fixed characteristic weight. This conception enabled Dalton to explain fully the fundamental laws of definite or fixed composition and multiple proportions.

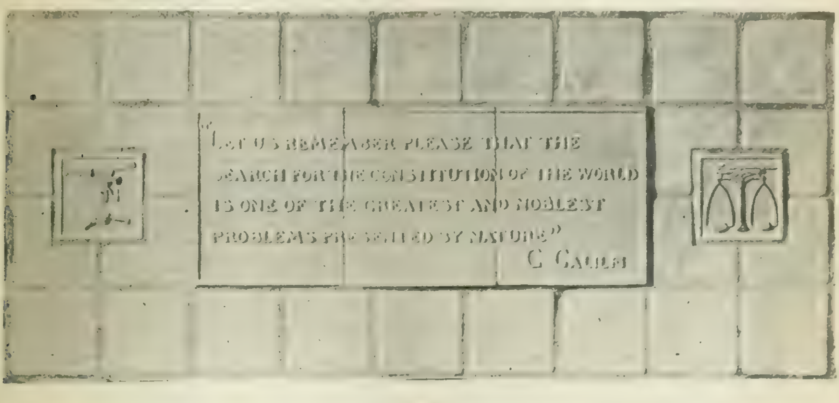
"Let us remember please that the
search for the constitution of the world
is one of the greatest and noblest
problems presented by nature"
G. Galilei

FIG. 2

In 1803 Dalton devised a symbolic notation for the elements and their compounds, which was both qualitative and quantitative. A circle with a dot at its center stood for one part by weight of hydrogen. A plain circle stood for the weight of oxygen (5.66 parts according to Dalton) which combined with one of hydrogen. The ten circular figures, five in each of two parallel vertical rows, one row on each side of the fountain, are Dalton's symbols for the most common elements: on the left—oxygen, iron, calcium, sodium, and potassium; on the right—magnesium, hydrogen, carbon, mercury, and sulfur.

A few years later Berzelius substituted for Dalton's geometrical hieroglyphic symbols, the more convenient and simple representation by letters now universally employed. Dalton's criticism of Berzelius' modification of his symbols is quaint: "Berzelius' symbols are horrifying; a young student in Chemistry might as soon learn Hebrew as make himself acquainted with them."

The achievements, both theoretical and practical, of the pure and applied chemistry of the Quantitative Period are far too numerous and extended for an outline. In fact, the chemistry lecture and laboratory courses of the universities of both hemispheres barely begin to convey an understanding of what chemistry is and what it does. Be this as it may, the fountain recognizes the function of chemistry's two foremost instruments, the spectroscope and the analytical balance, in promoting the motive of chemistry and other natural sciences. This motive, the motto of the fountain in the central horizontal panel, has been aptly expressed by Galileo Galilei, the inventor of the astronomical telescope, in the words, "Let us remember, please, that the search for the constitution of the world is one of the greatest and noblest problems presented by nature." (Fig. 2.)

To the left of this motto is the spectroscope, to the right the analytical balance. The use of the spectroscope in conjunction with the astronomical telescope reveals the constitution of the world. Practically every element known in the earth has been identified in the sun and in various heavenly bodies through spectro-photography and spectrum analysis. The delicacy of the spectroscopic test is the most extreme known, since it reveals the presence of one part of sodium vapor in twenty billion parts of air. This corresponds to our being able to detect a fragment of common salt weighing 0.00000000001 oz.!

On the other hand, the advent of the analytical balance enabled chemistry to become an exact science since through its use the quantitative composition of hundreds of thousands of compounds has been accurately determined. Specially constructed balances rival in sensitiveness the extreme delicacy of the spectroscope. For instance, Ramsay and Gray attacked the problem of determining the relation between the weight of an atom of the radium emanation, niton, and one of the rare gases, argon. This necessitated their making a balance capable of displacement from the central or zero position of balance when the minute load of a hundred-thousandth of a milligram is placed on it. This amounts to 0.00000004 oz. Thus Ramsay and Gray were able to deal with a very tiny bubble of niton weighing one fourteen-hundredth of a milligram, or about two-millionths of an ounce, and thereby show that the atomic weight of niton is about 222.

These facts serve to indicate how the spectroscope and the balance, only two of the chemist's numerous instruments, aid most substantially in the search for the constitution of the world, which, as Galilei states, is one of the greatest and noblest problems presented by nature. Undoubtedly, the extent of our knowledge of the constitution of the world and of matter, which also implies energy, determines the extent of the adaptability of both matter and energy to humanity's needs.

The Alchemists sought to make gold; the Iatrochemists to make medicines; the Phlogistonists, the immediate forerunners of chemistry as a quantitative science, sought more definitely for truth itself, which search culminates in an ethics of science. P. V. N. Myers in his "*History as Past Ethics*"[5] states that

> Among the particular virtues which science has fostered is philosophical veracity or love of truth. . . The man of science must be a truth-lover, a truth-seeker, and a truth-teller. He must take every pains to find out what is the exact fact, and then make a scrupulously veracious report of what he has found. It has in the creation of this scientific conscience, which pronounced the habit of accuracy, open-mindedness, impartiality of judgment, love of truth for truth's sake a supreme virtue, that science has rendered one of its greatest services to morality.

Thus Chemistry, pure and applied, the fundamental science of matter and energy transformations, may promote both the physical and the moral welfare of mankind. Its symbolism, as partially portrayed in the Rookwood fountain herewith described, readily lends itself to an artistic creation, which, it is hoped, will commemorate the good will of the donors of the fountain in establishing a university tradition and mark a unique achievement in ceramic craftsmanship serving as a symbolic outline of the history of chemistry.

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[5] Ginn & Co., **1913**, 353.

National Exposition of Chemical Industries

The following program of the 1922 Exposition supplements that given in the August issue of THIS JOURNAL and gives the plans as far as they have been completed. The dates for the meetings of the various chemical organizations are still only tentative.

Monday, September 11. 8:00 P. M.—Official Opening, Grand Central Palace Auditorium. Speakers, Wayne B. Wheeler, general counsel for the Anti-Saloon League; Charles H. Herty, chairman of the Exposition Committee and president of the Synthetic Organic Chemical Manufacturers Association of the United States; and others.

Tuesday, September 12. 2:00 P. M.—Program will probably be under the direction of the Synthetic Organic Chemical Manufacturers Association of the United States.

Wednesday, September 13. 2:00 P. M.—Program under the direction of the Technical Association of the Pulp and Paper Industry.

Thursday, September 14. 2:00 P. M.—Program under the direction of the Technical Photographic and Microscopical Society.

Friday, September 15. 2:00 P. M.—Program under the direction of the American Ceramic Society.

Friday Evening or Saturday, September 16.—A Symposium on Standardization.

All portions of the program held in the Grand Central Palace, with the exception of the dinners of various societies, will be open to all visitors at the Exposition. The annual dinners of the Salesmen's Association of the American Chemical Industry, and also that of the American Institute of Chemical Engineers, will be held on Wednesday evening, September 13. At the former, Herbert Hoover, Secretary of Commerce, will be the chief speaker. The Alpha Chi Sigma meets informally at dinner on Thursday, September 14.

The motion picture program includes the following in addition to those previously published:

The Story of Air Reduction. Courtesy of the U. S. Bureau of Mines.

The [illegible] Power at the Spanish River Pulp and Paper Company [illegible] Courtesy of the [illegible] H. Mead Company.

The Story of Natural [illegible]. Courtesy of the U. S. Bureau of Mines.

Dust Explosions. Courtesy of the U. S. Bureau of Chemistry.

Protozoa and Rotifers: Studies in Microscopic Animal Life. Courtesy of Philip O. Gravelle.

Extinguishing the Largest Oil Fire in the History of Casper, Wyoming.

Fire Extinguishing Tests on Blazing Oil Tanks at Port Arthur, Texas.

The All-Weather Fire Extinguisher That Won't Freeze.

An Industrial Firefoam Sprinkler System.

The last four films are the courtesy of the Foamite Firefoam Company.

Protecting Buildings against Lightning. Courtesy of Baltimore Copper Smelting and Rolling Company.

The program of the Technical Association of Pulp and Paper Industry and the Standardization program were given in full in August issue of THIS JOURNAL.

The program of the Technical Photographic and Microscopical Society is as follows:

Photomicrography in Pulp and Paper Research Problems. MISS ELOISE GERRY and E. M. DIEMER, Forest Products Laboratory, Madison, Wis.

The Photomicroscopy of Paint and Rubber Pigments. HENRY GREEN, New Jersey Zinc Co., Palmerton, Pa.

The Finishing of Motion-Picture Films. DOMINIC S. MUNGILLO, Craftsmen's Film Laboratory, New York.

Mechanics of Motion-Picture Apparatus. CLARENCE W. GIBBS, Victor Animatograph Co., New York.

The Motion Picture as an Aid to Industry. ALFRED B. HITCHINS, Director, Research Laboratory, Ansco Co., Binghamton, N. Y.

Microscopy in Leather Tanning. GUIDO E. DAUB, A. F. Gallun Sons Co., Milwaukee, Wis.

Use of the Microscope in Textile Work. ALBERT H. GRIMSHAW, Textile School, New Bedford, Mass.

Protozoa and Rotifers: Studies in Microscopic Animal Life. (Illustrated by motion pictures.) PHILIP O. GRAVELLE, South Orange, N. J.

The Federal Trade Commission has dismissed, without prejudice to its right to institute new proceedings, about forty complaints against nationally known business concerns which had been charged with maintaining resale prices similar to those in the Beech-Nut Packing Case. These cases were suspended until the determination of the Beech-Nut case, and in view of that decision and the age of the cases it has been decided to dismiss them and to institute new proceedings if new inquiries show it to be advisable.

WASHINGTON NOTES

Alleged Dye Monopoly Hearings

The much-discussed and long-awaited hearings before a subcommittee of the Committee on the Judiciary, United States Senate, pursuant to Senate Resolution 77, creating a special committee to investigate the expenditures made in behalf of various propaganda and in the maintenance of lobbies in Washington, have appeared under the caption "Alleged Dye Monopoly," and occupy 1485 pages of finely printed matter. If there exists a doubt in the mind of any chemist as to the existence of a monopoly in the domestic dye industry he should get a copy of these hearings and inform himself as to the true condition of affairs.

The hearings were begun on February 20, continued practically without interruption until May 16, and were finally concluded on June 3 when the committee met to hear some supplementary testimony. In nearly 1500 pages of testimony there is nothing to prove that there has been or is at present a monopoly in the dye and other branches of the organic chemical industry in the United States. The witnesses were examined under oath and waived any immunity under the law. The chairman of the subcommittee repeatedly invited cross-examination of the witnesses, but it is significant that in no instance was the invitation accepted.

From a study of this testimony it is evident that a grave injustice has been done the American dye industry by compelling the most prominent members of the industry to come to Washington, often at great personal sacrifice, expense and inconvenience, to answer trumped-up charges which are so obviously groundless and without foundation as to be absurd.

What Next?

The chemical industry seems to be suffering defeat all along the line, at least so far as the present tariff bill is concerned. By a vote of 32 to 30, the Senate rejected the recommendation of the Finance Committee to place a duty of 5 per cent ad valorem on chemical wood pulp and put it on the free list. Next came potash. Only one senator—Senator Shortridge—voted for a tariff. Senator McCumber then introduced an amendment which provided for a diminishing duty, similar in all respects to the tariff originally proposed except that the payment was transferred from the consumer to the U. S. Treasury. This amendment met with violent opposition on the floor of the Senate and was rejected by a vote of 32 to 27. This means that potash is keeping company with wood pulp on the free list. Now comes the vote on white arsenic which has likewise been placed on the free list. We cannot refrain from asking "What next?"

New Chemical Division

One of the chief aims of the newly organized Chemical Division of the Department of Commerce is to assist American chemical manufacturers by placing at their disposal accurate and detailed information on foreign markets for their products. The following branches of industry will be handled by this division:

Chemicals, general, organic and inorganic.
Dyes and coal-tar chemicals.
Pigments, paints, and varnishes.
Fertilizers and fertilizer materials.
Botanical drugs, pharmaceutical and medicinal preparations.
Essential oils, perfumery, cosmetics, and toilet preparations.
Explosives and fireworks.

The Department of Commerce is constantly receiving inquiries in regard to the introduction of American products into various foreign countries. The Chemical Division will serve as a medium to bring these opportunities promptly to the attention of domestic concerns. One of the first undertakings of the division will be the compilation of a list of domestic firms interested in the development of foreign trade. This list, known as the "Exporters Index," will serve as the basis of distribution of such information in foreign markets. The division also plans to organize advisory committees for each of the various branches of the chemical industry coöperating with the Department. In the case of existing trade associations, the contact with the industry will doubtless come through such associations.

The division will welcome suggestions from representatives in the industry by which it can be of assistance to domestic manufacturers.

Census of Dyes and Other Synthetic Organic Chemicals, 1921

The United States Tariff Commission has just issued as Tariff Information Series No. 26, a "Census of Dyes and Other Synthetic Organic Chemicals, 1921." There is included in this report for the first time a census of synthetic organic chemicals other than those derived from coal tar. The report shows a largely reduced output of dyes in 1921. This relatively limited production more nearly represents our domestic requirements, for the very high output of the previous year was coincident with a considerable export trade of the United States. This reduced output in 1921 may be accounted for by (1) the loss of most of our export trade, (2) the large stocks carried over from the previous year, and (3) the general business depression.

Congress Petitioned

The Synthetic Organic Chemical Manufacturers Association of the United States held a meeting in New York on August 4 for the purpose of discussing the situation now facing the American dye and organic chemical industry as a result of the action of the Senate in striking out of the tariff bill the protection proposed in the bill as submitted by the Finance Committee. As a result of an all-day discussion, the following petition was unanimously signed and forwarded to Senator McCumber, chairman of the Finance Committee, and to the other members of the Committee:

"At a meeting of the Synthetic Organic Chemical Manufacturers Association of the U. S., held at New York, August 4, 1922, the manufacturers of dyes, drugs and other organic chemicals, gave consideration to the serious danger that threatens their industry by reason of the defeat of the Dye and Chemical Control Act in the Senate, July 15. They now respectfully petition the Finance Committee to take such action as may be appropriate to reinstate the clauses in the Tariff Act stricken out by the Senate's action. They repeat what they have heretofore testified to before your Committee, that nothing less than the provisions of the Dye and Chemical Control Act will adequately protect their industry; that no specific or ad valorem rates will prevent the German Kartel from regaining absolute control of the American organic chemical market; and that the manufacture of dyes, medicinals, and other organic chemicals can no longer be maintained in this country without the legislative protection heretofore advocated by your Committee after thorough investigation of all the facts."

August 10, 1922

Calendar of Meetings

American Chemical Society—64th Meeting, Pittsburgh, Pa., September 4 to 9, 1922.

Eighth National Exposition of Chemical Industries—New York, N. Y., September 11 to 16, 1922.

American Electrochemical Society—42nd Meeting, Montreal, Canada, September 21 to 23, 1922.

American Institute of Mining and Metallurgical Engineers—126th Meeting, San Francisco, Calif., September 25 to 29, 1922.

American Society for Steel Treating—Convention, Detroit, Mich., October 2 to 7, 1922.

Paris Letter—Correction

In the letter from Mr. Charles Lormand appearing in the August issue of This Journal under the above title, the following correction is to be made on page 750:

In the paragraph on "The Commission on Chemical Periodicals" omit the expression reading, "(1) The abbreviations used by *Chemical Abstracts* are not desired" and substitute therefor the following: "For all abbreviations of titles of periodicals the abbreviations utilized by *Chemical Abstracts* are to be adopted."

BOOK REVIEWS

Fluidity and Plasticity. By E. C. BINGHAM. (International Chemical Series.) Cloth $8^1/_4 \times 5^1/_2$, xii + 440 pp., 96 illustrations. McGraw-Hill Book Co., Inc., New York, 1922. Price, $4.00.

In 1914 Dunstan and Thole could cover the relation between viscosity and chemical composition, and related subjects, in 89 pages, while Bingham, largely on account of his own pioneer work in plasticity, now needs 429 pages. Bingham's predilection for fluidity makes him less thorough in considering the technical measurement of high viscosities. Thus (p. 35) there is no reference to the change in critical velocity with the length of capillary, and (p. 69) the directions for selecting a viscometer do not apply to oils, for which the maximum viscosity must be considered. The statement (p. 233) that the rate of flow through an orifice is independent of the fluidity is evidently inapplicable to liquids of high viscosity. The conclusion (p. 29) is also open to question, that as the Couette correction has no definite value it is unnecessary to determine where it should be applied. The value has been found to vary with the conditions, although the average value may approach zero. (W. F. Higgins, "Collected Researches," National Physical Laboratory; Bureau of Standards, *Technical Paper* 112.) When the Couette correction is ignored, an accuracy of 0.1 per cent (p. 65) cannot be obtained without an excessively long capillary, even if other errors are assumed negligible.

The reader who is interested in plasticity should perhaps consult the original papers and form his own judgments. (The bibliography of 82 pages should prove of great value for this and other purposes.) Bingham's contention (p. 225) that conditions should be controlled so that all the observed points lie on a straight line, is a help as far as calculation is concerned, but may lead to misinterpretation if, as Buckingham has indicated, there are three properties of the material to be measured, just as the assumption of the one property of "viscosity" for a plastic material has caused endless confusion.

WINSLOW H. HERSCHEL

Colloid Chemistry of the Proteins. Part I. By WOLFGANG PAULI, translated by P. C. L. THORNE. Cloth, $8^1/_2 \times 5^1/_2$, xii + 140 pp. P. Blakiston's Son & Co., Philadelphia, 1922. Price, $2.25 net.

This book is the first part of a small volume developed from lectures delivered during the winter of 1912–13 and from such work of others as seemed desirable to the author in rounding off the presentation. Part II is scheduled to appear within a year.

After a brief introduction to colloid chemistry, the author treats the soluble proteins, in particular the albumins, as amphoteric electrolytes, each having two mean ionization constants, one as an acid and the other as a base, which characterize it. This view forms the basis of a very illuminating discussion on the behavior of albumins in solutions of acids and bases and at the isoelectric point. Issue is taken with Robertson's view that both [illegible] are formed. Electrophoresis experiments on albumin solutions show only positively [illegible] in alk[illegible] form. The book closes with an interesting discussion of the migration velocity of protein ions.

With the rise of colloid chemistry, it has become evident that the reactions of the proteins follow well-known laws of physical chemistry. Since the author appreciates this, it is regrettable that he is not more thoroughly familiar with the works of Procter and Loeb, which would have enabled him to avoid dependence upon the assumption that low concentrations of electrolyte markedly repress the ionization of protein salts or that increased viscosity of protein solutions is necessarily due to the hydration of protein ions. However, the remarkably clear presentation of certain phases of the subject establishes the book as a valuable contribution to the literature on the physical chemistry of the proteins.

JOHN ARTHUR WILSON

Reports of the Progress of Applied Chemistry. Issued by the SOCIETY OF CHEMICAL INDUSTRY. Vol. VI, 1921. 625 pp. Society of Chemical Industry, Central House, 46/47 Finsbury Square, London, E. C. 2.

This publication, now appearing for the sixth consecutive year, has proved itself a most welcome friend to one who would keep himself informed of what is going on in the many fields of chemical activity. No one can hope to cover all the fields and often his own specialty is all he can hope to do in detail. But here some twenty-six subjects are covered by as many different specialists who have assembled a valuable résumé. Not only is the literature covered broadly from English, American, French, German, and other sources but references are given to the patent literature and to patents issued.

In many chapters the plan of review is systematic, broad, and comprehensive in its arrangement and execution. The extent of the field that is covered is shown by the following chapter headings: Plant and Machinery; Fuel; Gas, Destructive Distillation, Tar Products; Mineral Oils; Coloring Matters and Dyes; Fibers, Textiles, Cellulose and Paper; Bleaching, Dyeing, Printing, and Finishing; Acids, Alkalies, Salts, etc.; Glass; Refractory Materials; Ceramics and Building Materials; Iron and Steel; Metallurgy of the Nonferrous Metals; Electrochemical and Electrometallurgical Industries; Oils, Fats and Waxes; Paints, Pigments, Varnishes and Resins; India Rubber; Leather and Glue; Soils and Fertilizers; Sugars, Starches and Gums; Fermentation Industries; Foods; Sanitation and Water Purification; Fine Chemicals, Medicinal Substances, Essential Oils; Photographic Materials and Processes; Explosives.

A chapter headed Analytical Chemistry that appeared in last year's Reports is omitted this year (1922), and the heading heretofore Agricultural Chemistry has been changed to Soils and Fertilizers, although the subject matter is along the lines of the previous chapters on Agricultural Chemistry in preceding volumes. At the conclusion of the subject matter are two indexes—one a name index, the other a subject index, each apparently quite complete and correct.

Not only is the book interesting even to one with a slight knowledge of chemistry and its application to the arts and manufactures, but to the various specialists in many, if not in all, subjects there will be some hint or suggestion of a new fact or discovery.

Altogether it is a worth-while book which ought to be widely distributed in chemical libraries, and the equal of its predecessors.

R. L. EMERSON

Industrial Oil Engineering, Lubrication and Industrial Oil Section. By JOHN ROME BATTLE, B.Sc. in M.E. 1131 pp. J. B. Lippincott, Philadelphia and London, 1920. Price, $10.00.

This reference book contains a collection of tables and miscellaneous data relating to industrial oils, mainly lubricants. Although the reviewer realizes the great labor and difficulties connected with the compilation of data from numerous sources, he feels that the value of the book would have been considerably increased if more care had been used in the selection and arrangement of the material. Some of this is of very doubtful value, as, for instance, the obsolete and partly incorrect conversion table for weights and measures (p. 26). It may be interesting to know the method used by African natives to produce palm oil (p. 252), or the color of the funnels of the Cunard line steamers (p. 781); to the reviewer, however, these matters appear irrelevant to the subject of the book, and the space might have been better occupied, for instance, by a definition of kinematic viscosity, repeatedly mentioned in the book.

A good many repetitions and duplications are found in the book, which tend to swell the volume and hide its good points. Thus, the Conradson carbon test is described three times, twice at page 322 and again at page 1051. That sodium and potassium hydroxides are known as alkalies, is pointed out twice, on pages 230 and 876.

More serious than the above are some statements that are directly misleading: Temporary hardness of water is ascribed to calcium and magnesium carbonates (p. 73). Pale paraffin oil (mineral soap oil) is declared on page 876 to be capable of neutralizing an amount of caustic or carbonate in the soap kettle.

The book will be found useful in many respects, despite shortcomings of the kind mentioned above, which should be eliminated in a future edition. The printing and other mechanical features of the book are excellent.

Synthetic Tannins: Their Synthesis, Industrial Production and Application. GEORG GRASSER, Lecturer in Tanning Chemistry at the German Technical College, Brunn. Translated into English by F. G. A. ENNA. viii + 143 pp. D. Van Nostrand Co., New York, 1922. Price, $4.00.

The German edition of this useful book was written in 1920 by Grasser, who should be an authority on syntans as a result of his work in this field for the Badische Anilin und Soda-Fabrik.

Syntans have received considerable attention since the Great War. There is no doubt that syntans were "life-savers" to German leather manufacture when the Central Empires were cut off from sources of vegetable tanning materials. In the author's German preface is stated, "Just as in the case of the coal-tar dyes, the synthetic tannins will make us independent of foreign supplies, and thus keep within our borders the vast sum of money required in former days for the purchase of foreign tanning materials."

The book is divided into two parts. Part I, consisting of 77 pages, deals with (*a*) synthesis of vegetable tannins and depsides, (*b*) synthesis of tanning matters by condensation of phenols, hydroxybenzenes, naphthalene derivatives, and the anthracene, and di-, and triphenylmethane groups, (*c*) tanning effects of mixtures and natural products, and (*d*) methods of examination of tanning matters. Part II, 60 pages, deals with syntans, predominately Neradol D, their industrial production, application, and properties.

A number of syntans are not mentioned, but it is natural, in view of the author's connection, that Badische products should be discussed to the exclusion of other manufacturers' products.

This book contains much information that is useful for the practical tanner as well as for the tannery and organic chemist.

A. W. THOMAS

Fuel and Refractory Materials. By A. HUMBOLDT SEXTON, F.I.C., F.C.S., completely revised and enlarged by W. B. DAVIDSON, D.Sc., PH.D., F.I.C. 382 pp., 111 illustrations. D. Van Nostrand Co., New York, 1921. Price, $4.00.

Whoever undertakes to write a book on industrial chemistry in any of its phases must meet squarely the task of describing up-to-date practice, for by so much as he fails in this his labor is in vain. In "Fuel and Refractory Materials" the reviser seems to have had indifferent success in this respect. Though a Briton and stressing British methods, he strives, apparently, to be eclectic in the treatment of his subject, and the best general practice must therefore be the basis for judging his book.

American charcoal manufacture is discussed from the standpoint of a method used in 1876 employing the bee-hive type of oven; no reference is made to the modern continuous retort oven with its extensive plant for the treatment of by-products. The only journal reference is dated 1883.

The subject of powdered fuel is given a short paragraph in description of experimental work done between 1873 and 1896. Is it possible that the author has not heard of the tremendous development of this branch of fuel technology since that period? With one exception the methods of coal calorimetry given are obsolete, or should be at least. The Berthelot-Mahler is illustrated with a cut of one of the crude early forms of this instrument.

Shale oils and distilled petroleums are given half a page each, mention being confined to Scotch shales and to Pennsylvania and Baku crudes, respectively, while under the head of motor spirit nothing is said of cracking processes. Recent views of the constitution of coal and some modern theories of the chemistry of coking "have not been incorporated, as it is felt that these subjects are still in their infancy."

In spite of many excellent features of the book, the reviewer feels that without liberal use of the blue pencil in the hands of the instructor it cannot be used as a textbook for students; as a reference book for the industries, it is on the whole too superficial to be of great value.

H. L. OLIN

Metric System for Engineers. By CHARLES B. CLAPHAM, Lecturer in Engineering, University of London. 181 pp. E. P. Dutton & Co., New York, 1922. Price, $6.00.

This book, as the author states in his preface, is designed to offer a thorough exposition of the metric system, particularly as it is met with in engineering calculations and measurements. After an introduction, in which the fundamental principles of the system are explained, the measurements of length, area, volume, and weight are fully treated in separate chapters. Well-arranged tables of equivalents are given in each topic, together with numerous practical problems, showing how the metric system is employed in a great variety of engineering calculations. A chapter is devoted to measurements of energy and work, acceleration, power and heat, in which appear the less common units of measurement, which are often confusing to those who are unacquainted with their derivation. The last chapter presents an impartial review of the controversy which has arisen in England and the United States over the adoption of the metric system. Such topics as the complexity of the present English system, the origin and growth of the metric system, its present position in Great Britain and in this country, and the important question of the practicability of its adoption are treated in a very interesting manner. In spite of the apparent painstaking effort of the author to present both sides of the question from the viewpoint of an engineer, this chapter as a whole presents one of the best general arguments for the adoption of the metric system which the reviewer has seen. A careful reading of the book reveals very few typographical or other errors. It will be especially useful to all who are not fully acquainted with the system and who have occasion to apply it in engineering or other industrial lines of work.

ROBERT E. SWAIN

CURRENT PUBLICATIONS

NEW BOOKS

A[illegible]n F[illegible]. [illegible] F. Bacon and William A. Hamor. Mellon Institute Technochemical Series. Vol. I. 630 pp. Vol. II. 615 pp. Illustrated. Price, $12.00 per set, net. Not sold separately. McGraw-Hill Book Co., Inc., New York.

Analytical Chemistry: Calculations of Analytical Chemistry. E. H. Miller. 201 pp. Price, 9s. Macmillan & Co., Ltd., London.

Analytische Chemie der Alkaloide. K. H. Bauer. 425 pp. Price, $4.80. Gebruder Borntraeger, Berlin.

Adhesives: First Report of the Adhesive Research Committee. 129 pp. Price, 4s. $2^1/_2$d. H. M. Stationery Office, London.

The British Association. A Retrospect 1831–1921. O. J. R. Howarth. 318 pp. Price, 7s. 6d. The British Association for the Advancement of Science, London.

Chemistry for Beginners and Schools. C. T. Kingzett. 237 pp. Price, [illegible] Baillière, Tindall & Cox, London.

Chemistry: A First Book of Chemistry for Students in Junior Technical Schools. A. Coulthard. 156 pp. Price, $1.25. Isaac Pitman & Sons, New York.

Chemistry: Second Year College Chemistry. A Manual of Laboratory Exercises. William H. Chapin. 122 pp. Illustrated. Price, $1.50. D. Van Nostrand Co., New York.

Coal: Mitteilungen aus dem Schlesischen Kohlenforschungsinstitut der Kaiser-Wilhelm Gesellschaft. Fritz Hofmann. 180 pp. Price, $3.50. Gebruder Borntraeger, Berlin.

Coal-Tar Colors in the Decorative Industries. A. Clarke. 166 pp. Price, [illegible] net. Constable & Co., Ltd., London.

Colloids: Les Colloides. J. Duclaux. 2nd edition, revised and enlarged. 305 pp. Price, 10 fr. Gauthier-Villars et Cie, Paris.

Copper: Les Progrès de la Métallurgie du Cuivre. A. Conduché. Encyclopédie Léauté. 254 pp. Price, 14 fr. Masson et Cie., Paris.

Dictionary: Werkstoffe: Handwörterbuch der Technischen Waren und ihrer Bestandteile. Paul Krais et al. 3 volumes. 529, 784, and 728 pp. Price, paper [illegible] mk., bound 540 mk. J. A. Barth, Leipzig.

Fats: Die Losungsmittel der Fette, Oele, Wachse und Harze. H. Wolff. Monographs on the Chemistry of Fats, edited by K. H. Bauer. 118 pp. Price, 9s. Wissenschaftliche Verlagsgesellschaft, Stuttgart.

Fuel: Report of the Fuel Research Board for the Years 1920, 1921. Second Section. Low Temperature Carbonization. Department of Scientific and Industrial Research. 73 pp. Price, 2s. H. M. Stationery Office, London.

Fur Dyeing and Fur Dressing. William E. Austin. 191 pp. Price, $4.00. D. Van Nostrand Co., New York.

Handbook: A Pocketbook for Chemists. T. Bayley. 425 pp. Price, $[illegible] [illegible], New York.

Intermediate Chemistry: Smith's Intermediate Chemistry. James Kendall and E. E. Slosson. 566 pp. Price, $3.25. The Century Co., New York.

Intermediate Chemistry: A Laboratory Outline of Smith's Intermediate Chemistry. James Kendall. 127 pp. Price, $1.25. The Century Co., New York.

Minerals: Essentials for the Microscopical Determination of Rock-Forming Minerals and Rocks, in Thin Sections. Albert Johannsen. 53 pp. Illustrated. Price, $2.00. University of Chicago, Chicago.

Modern Chemical Lecture Diagrams. Geoffrey Martin. 88 pp. Price, [illegible] Low, Marston & Co., Ltd., London.

Nitrogen Fixation: L'Azote: La Fixation de l'Azote Atmosphérique et son [illegible] Encyclopédie Léauté. 271 pp. Price, 14 fr. Masson et Cie., Paris.

[illegible] and P. C. R. [illegible]. [illegible] pp. Price, 7s. 6d. University of London Press, London.

Organic Chemistry: Theories of Organic Chemistry. Ferdinand Henrich. Translated and enlarged from the 4th revised German edition by [illegible]

P[illegible] Manufacture, a Complete [illegible] and Cosmetic Manufacture [illegible] Essential Oil and Other **Perfume Materials, the Compounding of Perfumes and the Perfuming** of [illegible] Price, [illegible]

Photography: Abridged Scientific Publications from the Research Laboratory of the Eastman Kodak Co. No. 4. 319 pp. Eastman Kodak Co., Rochester, N. Y.

Petroleum: Handbook of the Petroleum Industry. David T. Day, *et al.* Two volumes. 2070 pp. Price, $15.00, net. John Wiley & Sons, Inc., New York.

Quantitative Analysis: Calculations of Quantitative Chemical Analysis. L. F. Hamilton and S. G. Simpson. 191 pp. Price, $2.00. McGraw-Hill Book Co., Inc., New York.

Relativity: The Theory of General Relativity and Gravitation. Ludwik Silberstein. 141 pp. Price, $2.00. D. Van Nostrand Co., New York.

Steel Foundry. John Howe Hall. 2nd edition, revised and enlarged. 334 pp. Illustrated. Price, $4.00. McGraw-Hill Book Co., Inc., New York.

Tanning: Manuel du Tanneur, Mégissier, Corroyeur. P. Huc. Bibliothèque Professionnelle. 402 pp. Price, 12 fr. net. J. B. Baillière et Fils, Paris.

Textiles and Their Manufacture. A. F. Barker, W. M. Gardner, R. Snow, and F. Bradbury. 386 pp. Illustrated. Price, 15s. net. Constable & Co., Ltd., London.

RECENT JOURNAL ARTICLES

Ammonia: Transformation Industrielle de l'Ammoniaque en Urée, Engrais de Haute Concentration. Camille Matignon. *Chimie et industrie,* Vol. 7 (1922), No. 6, pp. 1057–70.

Blast Furnace: The Development of the Blast Furnace. J. Henderson. *Journal of the Chemical, Metallurgical, and Mining Society of South Africa,* Vol. 22 (1922), No. 10, pp. 178–83.

Colloids in Geologic Problems. George D. Hubbard. *American Journa of Science,* Vol. 4 (1922), No. 20 (Whole No. 204), pp. 95–110.

Chrome Tanning, X. Modern Problems in Chrome Tanning. Donald Burton. *Journal of the Society of Leather Trades' Chemists,* Vol. 6 (1922), No. 7, pp. 226–34.

Dyeing Apparatus: A Consideration of the Various Substances Used in the Construction of Dyeing and Bleaching Utensils and Apparatus. H. Grandage and W. E. Hadley. *American Dyestuff Reporter,* Vol. 11 (1922), No. 2, pp. 41–42; No. 3, pp. 73–75.

Fuel Economy in Heating Furnaces. K. Huessener. *The Blast Furnace and Steel Plant,* Vol. 10 (1922), No. 7, pp. 380–83.

Fuels: The Influence of Structure on the Combustibility and Other Properties of Solid Fuels. E. R. Sutcliffe and Edgar C. Evans. *Journal of the Society of Chemical Industry,* Vol. 41 (1922), No. 12, pp. 196T–208T.

Gas: Effect of B. t. u. on Burner Efficiency. Messrs. Berry, Brumbaugh, Eiseman, Moulton and Shawn. *Gas Age-Record,* Vol. 50 (1922), No. 2, pp. 41–44, 46–48; No. 3, pp. 81–84.

Glass: Disintegration of Soda Lime Glasses in Water. Arthur E. Williams. *Journal of the American Ceramic Society,* Vol. 5 (1922), No. 8, pp. 504–17.

Metals: Heat-Temperature Curves of Metals. Joseph F. Shadgen. *The Iron Age,* Vol. 110 (1922), No. 4, pp. 218–22.

Nonferrous Metals: Gas Absorption and Oxidation of Nonferrous Metals. B. Woyski and John W. Boeck. *The Metal Industry,* Vol. 20 (1922), No. 8, pp. 307–08.

Plasticity: Mechanism of Plasticity from Colloid Standpoint. G. A. Bole. *Journal of the American Ceramic Society,* Vol. 5 (1922), No. 8, pp. 469–77.

Research from the Business Man's Standpoint. Edward P. Hyde. *Chemical Age,* Vol. 30 (1922), No. 7, pp. 289–91.

Rubber: The Coefficient of Vulcanization of Rubber. G. Martin and F. L. Elliott. *Journal of the Society of Chemical Industry,* Vol. 41 (1922), No. 13, pp. 225T–28T.

Rubber: Measuring the Size of Pigments Used in Rubber Manufacture. A. D. Luttringer. *The Rubber Age,* Vol. 11 (1922), No. 8, pp. 277–79. Translated from *Le Caoutchouc et la Gutta Percha.*

Scale Formation and Corrosion in Boilers. Alan A. Pollitt. *The Chemical Age* (London), Vol. 7 (1922), No. 162, pp. 76–78.

Steel: The Decomposition of Martensite into Troostite in Alloy Steels. Howard Scott. *Forging and Heat Treating,* Vol. 8 (1922), No. 7, pp. 296–99.

Steel: Rapid Methods for the Determination of Chromium in Steel. A. S. Townsend. *Forging and Heat Treating*, Vol. 8 (1922), No. 7, pp. 304–05.

Vanillin: La Vanilline. P. Alexandre and J. Martinet. *Chimie et Industrie*, Vol. 7 (1922), No. 6, pp. 1043–56.

Waterproofing by Electricity. Ismar Ginsberg. *Color Trade Journal*, Vol. 11 (1922), No. 1, pp. 1–6.

GOVERNMENT PUBLICATIONS

Notice—*Publications for which price is indicated can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C. Other publications can usually be supplied from the Bureau or Department from which they originate.*

Bureau of Chemistry

The Bureau of Chemistry of the Department of Agriculture. Organization, Enforcement of Food and Drugs Act, Enforcement of Tea Act, Research Work. *Department Circular* **137**, revised. 23 pp. Paper, 5 cents.

Home Tanning. R. W. Frey, I. D. Clarke, and F. P. Veitch. *Department Circular* **230.** 22 pp. Paper, 5 cents. Issued July 1922.

Bureau of Foreign and Domestic Commerce

Copra and Coconut Oils in Netherlands, East Indies and British Malaya. J. A. Fowler. *Trade Information Bulletin* **34.** Foodstuffs Division. Published June 19, 1922. 12 pp.

Finland's Paper and Pulp Industries. L. A. Davis. *Trade Information Bulletin* **33.** Paper Division. 12 pp. Published June 19, 1922.

Bureau of Mines

Application of the Geophone to Mining Operations. Alan Leighton. *Technical Paper* **277.** 33 pp. Paper, 10 cents.

Coal-Mine Fatalities in the United States 1921. W. W. Adams. *Technical Paper* **302.** 72 pp. Paper, 10 cents.

Determination of Suspended Matter in Gases by Collection on Filter Paper. S. H. Katz and G. W. Smith. *Reports of Investigations* **2378.** 6 pp. Issued July 1922.

Explosives Used in May 1922. W. W. Adams. *Reports of Investigations* **2376.** 5 pp. Issued July 1922.

Factors in the Spontaneous Combustion of Coal. O. P. Hood. *Technical Paper* **311.** 9 pp. Paper, 5 cents.

Bureau of Standards

Durability of Cement Drain Tile and Concrete in Alkali Soils. Third Progress Report 1919–1920. G. M. Williams in coöperation with R. J. Wig, S. H. McCrory, E. C. Bebb, L. R. Ferguson, C. J. MacKenzie, D. A. Abrams and G. E. Warren. *Technologic Paper* **214.** 32 pp. Paper, 10 cents.

United States Government Specification for Green Paint, Semipaste and Ready Mixed, Federal Specifications Board, Standard Specification 15. Officially Adopted by Federal Specifications Board, February 3, 1922, for Use of Departments and Independent Establishments of the Government in the Purchase of Materials Covered by It. *Circular* **97.** 2nd ed. 10 pp. Paper, 5 cents.

United States Government Specification for Red Lead, Dry and Paste, Federal Specifications Board, Standard Specification 11. Officially Adopted by Federal Specifications Board February 3, 1922, for Use of Departments and Independent Establishments of the Government in the Purchase of Materials Covered by It. *Circular* **90.** 2nd ed. 8 pp. Paper, 5 cents.

Bureau of the Census

Gypsum: 14th Census of the United States: Mines and Quarries, 1919. Prepared under the supervision of E. F. Harley by F. J. Katz. 10 pp. 1922.

Stone: 14th Census of the United States: Mines and Quarries, 1919. Prepared under the supervision of E. F. Harley by F. J. Katz. 31 pp. 1922.

Turpentine and Rosin: 14th Census of the United States: Forest Products, 1919. Prepared under the supervision of E. F. Harley. 10 pp. 1922.

Congress

Alleged Dye Monopoly. Hearings before a subcommittee of the Committee on the Judiciary, United States Senate, pursuant to S. Res. 77 creating a special committee to investigate the expenditures made in behalf of various propaganda and in the maintenance of lobbies in Washington. 1485 pp. 1922.

Linseed Oil. A bill to provide for an emergency tariff to be levied on all linseed oil coming into the United States from foreign countries, and for other purposes. Introduced by Mr. Ladd, July 12, 1922, and referred to the Committee on Finance. S. 3814. 2 pp.

Muscle Shoals. Hearings before the Committee on Agriculture and Forestry United States Senate on S. 3420 to provide for the manufacture of explosives for the use of the Army and Navy, to provide for the manufacture of fertilizer for agricultural purposes, to incorporate the Federal Chemical Corporation, and for other purposes; and on the Henry Ford Muscle Shoals offer; offer made by the Alabama Power Co., proposing to complete Wilson Dam; offer of Frederick E. Engstrum for Muscle Shoals; and offer of Charles L. Parsons for properties at Muscles Shoals, Ala. Part 4. 346 pp. 1922.

Muscle Shoals. Minority views to accompany H. R. 11903 [to authorize the Secretary of War to sell to Henry Ford nitrate plant numbered 1, at Sheffield, Ala., nitrate plant numbered 2, at Muscle Shoals, Ala., Waco quarry, near Russellville, Ala., and to lease to corporation to be incorporated by him dam numbered 2 and dam numbered 3 (as designated in H. Doc. 1262, 64th Congress, 1st session), including power stations when constructed as provided herein]. Submitted by Mr. Kearns June 20, 1922. *H. Rp.* **1084.** Part 2. 12 pp.

Geological Survey

Advance Statement of the Production of Copper in the United States in 1921. H. A. C. Jenison. 4 pp. 1922.

Asbestos in 1920. Edward Sampson. Separate from Mineral Resources of the United States, 1920, Part 2. 14 pp. Published July 7, 1922.

Asphalt and Related Bitumens in 1921. K. W. Cottrell. Separate from Mineral Resources of the United States, 1921, Part 2. 7 pp. Published July 26, 1922.

Carbon Black Produced from Natural Gas in 1921. E. G. Sievers. Separate from Mineral Resources of the United States, 1921, Part 2. 5 pp. Published July 5, 1922.

Fluorspar and Cryolite in 1921. H. W. Davis. Separate from Mineral Resources of the United States, 1921, Part 2. 12 pp. Published July 6, 1921.

Fuller's Earth in 1921. Jefferson Middleton. Separate from Mineral Resources of the United States, 1921, Part 2. 2 pp. Published June 16, 1922.

Gold and Silver in 1920 (General Report). J. P. Dunlop. Separate from Mineral Resources of the United States, 1920, Part 1. 38 pp. Published June 23, 1922.

Gold, Silver, Copper, Lead, and Zinc in Colorado in 1920. Mines Report. C. W. Henderson. Separate from Mineral Resources of the United States, 1920, Part 1. 31 pp. Published July 6, 1922.

Lead and Zinc Pigments and Salts in 1921. C. E. Siebenthal and A. Stoll. Separate from Mineral Resources of the United States, 1921, Part 1. 8 pp. Published July 10, 1922.

Manganese and Manganiferous Ores in 1921. H. A. C. Jenison. Separate from Mineral Resources of the United States, 1921, Part 1. 10 pp. Published July 8, 1922.

Phosphate Rock in 1921. K. W. Cottrell. Separate from Mineral Resources of the United States, 1921. 4 pp. Published July 11, 1922.

Potash in 1921. M. R. Nourse. Separate from Mineral Resources of the United States, 1921, Part 2. 13 pp. Published July 10, 1922.

Slate in 1921. G. F. Loughlin and A. T. Coons. Separate from Mineral Resources of the United States, 1921, Part 2. 8 pp. Published June 29, 1922.

Public Health Service

A Source of Lead Contamination of Cistern Water. Report of an Examination of the Drinking Water Supply System at the U. S. Fish Hatchery Station, Ten Pound Island, Gloucester, Mass., for Possible Sources of Lead Contamination. Leonard Greenburg. *Public Health Reports* **37** (July 28, 1922), 1825–9.

Control of Drinking and Culinary Water on Vessels in Interstate Traffic. The Supervision and Control of Water Provided for Drinking and Culinary Purposes on Vessels Operating in Interstate Traffic on the Great Lakes and Ohio River during the Navigation Season of 1921, as Exercised by the United States Public Health Service in Coöperation with State and Local Health Authorities. A. E. Gorman. *Public Health Reports* **37** (June 30, 1922), 1573–80.

The Relative Parasiticidal Value of Arsphenamine and Neoarsphenamine. With a Description of the Trypanocidal Test. Carl Voegtlin and D. W. Miller. *Public Health Reports* **37** (July 7, 1922), 1627–41.

Tariff Commission

Census of Dyes and Other Synthetic Organic Chemicals, 1921. Tariff Information Series 26. 174 pp. Paper, 15 cents. 1922.

MARKET REPORT—AUGUST, 1922

[SUPPLIED BY DRUG & CHEMICAL MARKETS]

Chemical prices generally are extremely nervous and several important items have been sharply advanced during the month past. The gradual absorption of the government surplus stocks of phenol has finally resulted in an acute shortage and prices are extremely firm. Nothing better than 15 cents per pound could be done after August first for carlots of large drums, which is the price asked by the refiners of natural on the same quantity of material. No synthetic phenol has been made for the past two years and the government surplus has been the sole dependence of consumers. The virtual demolition of this surplus has left the market in an extremely tight position, with little prospect of relief until it is possible for makers of synthetic to get their plants back into operation, which will take some time, according to reports now current in the trade. Following this condition makers of salicylates advanced their prices sharply and are now looking forward to a real shortage for lack of raw material.

An advance of 35 cents per hundred was made by the makers of calcium acetate late in July, making the new price $2.35 per hundred at the works. This, following as it did an advance early in July, forced a further advance in acetic acid, and thus greatly discouraged buyers, who were already none too insistent. The present prices of acetic acid are based on $2.67^1/_2$ for 28 per cent in carlots of barrels at makers' works, and many of the consumers of this product consider this level too high for safe buying. The consequence has been a general reduction of purchases throughout the market. Acetone and methyl ethyl ketone were advanced correspondingly.

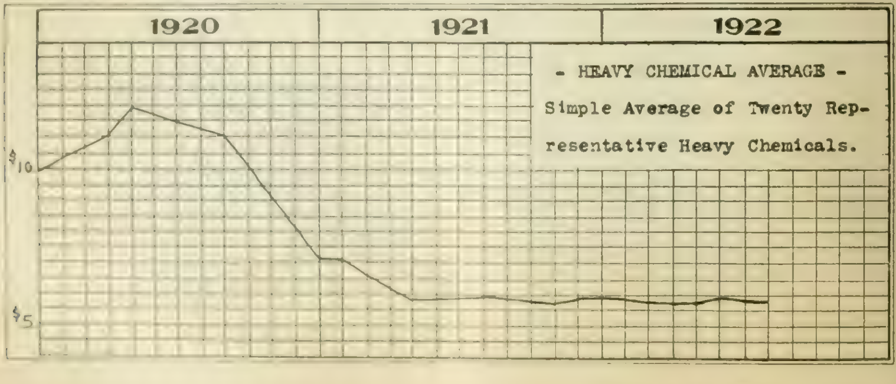
Glycerol has been advanced by makers during the period and is firm at the higher level. Camphor has been firmer and higher from Japan. Oxalic acid has been in good demand throughout the period and has been twice advanced by makers to a present level of 16 cents at their works. In one direction it has been found possible to shade this figure somewhat, but the general attitude is one of firmness.

In the inorganic list, interest has been centered largely in the insecticide situation. Copper sulfate continues extremely scarce, and few firm offers are available, even at the nominal price of 7 cents named in a few cases for odd lot business. Arsenic is becoming increasingly attractive to many speculative and consuming interests. Reports from the cotton-growing districts state that the demand for insecticides for the present season has not been satisfied yet, on account of the coming of a veritable plague of the cotton leaf worm from the Mexican border. The call from the affected districts is for any arsenical compound that can be used for checking its spread. This demand comes at a time when makers have practically nothing to offer in either calcium arsenate, lead arsenate, or Paris green, and when the white arsenic market is attracting speculative buyers in such numbers as at present. The coming of real consuming demand is forcing prices rapidly higher. So far there have been few sales above 8 cents, but many indications point to further advances. The lack of activity in the copper-producing areas, from which the domestic arsenic supply comes, the higher prices asked from Japan for shipments, and the dearth of supplies in any of the other markets of the world, are taken as the basis of extremely bullish reports which are being widely circulated in the market.

Many of the large consumers of chemical materials have established rules that no supplies shall be taken on under any circumstances which are not immediately needed in plant operations. This has led to frequent irregular telegraphic orders for rush shipments to be delivered within a few hours at most, and has greatly confused the situation. Indications point to sharp advances on the slightest provocation. Declines may be caused in a similar way by the forced release of any considerable quantity of material by speculators or others who are not in position to hold for favorable sale.

The coal-tar product situation generally has attracted little additional interest from the trade during the past month. Plans are being made by the larger interests in intermediates and dyes to continue operations whether the licensing feature of the tariff bill is included or not. Consumers in the meantime are taking on only such limited supplies as are required for their present requirements. Less tendency is noted among manufacturers to cut prices on this small lot business and there are many features of firmness in the situation, but the total amount of business being done is small.

Fertilizer materials are stronger in all markets on short supplies in the face of increasing demand for export. Vegetable oils have shown little strength during the month on declining prices on cottonseed oil. Prospects in this oil indicate a heavy yield from the present crop and consequently lower prices. Fish oils are firm. Menhaden oil is particularly firm and scarce on account of the low yield from the poor catch caused by poor weather conditions during the fishing season. Animal oils are little changed and have shown a fairly steady trend. Turpentine has reached a steady level after the sharp speculative advances of a short time ago. The trend of the metal markets has been upward, although the actual net increases have not been large.



Courtesy of Drug & Chemical Markets

FIRST-HAND PRICES FOR GOODS IN ORIGINAL PACKAGES PREVAILING IN THE NEW YORK MARKET

INORGANIC CHEMICALS

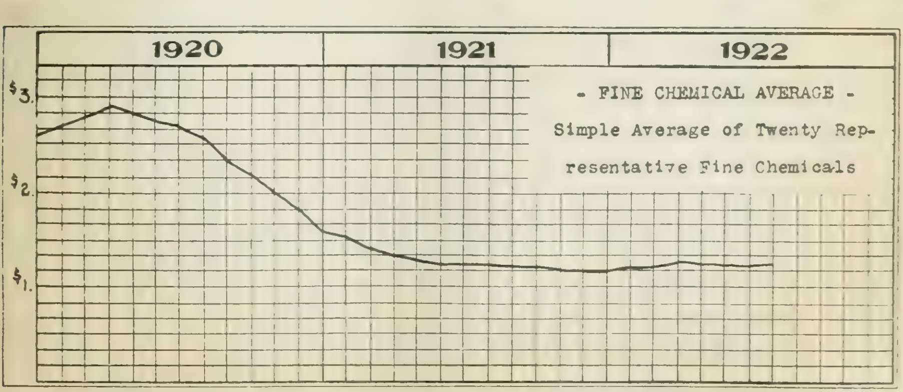
	Aug. 1	Aug. 10	Jan. 1922
Acid, Boric, cryst. bbls . . . lb.	.11¾	.11¾	.12¾
Hydrochloric, comm'l. 20° lb.	.01¼	.01¼	.01¼
Hydrofluoric, 30% bbls. . lb.	.07	.07	.07
Hydriodic, sp. gr. 1.150 . . . lb.	2.25	2.25	2.00
Nitric, 42°, cbys. c/l wks. lb.	.06	.06	.06
Phosphoric, 50% tech. . . . . lb.	.08	.08	.10
Sulfuric, C. P. . . . . lb.	.07	.07	.07
66° tks. wks. . . . . ton	16.00	16.00	16.00
Oleum 20% . . . . ton	19.00	19.00	19.00
Alum, Ammonia, lump . . . . lb.	.03½	.03½	.03½
Potash, lump . . . . lb.	*.03	*.03	*.03½
Chrome . . . . lb.	.06½	.06½	.07
Soda, ground . . . . lb.	.03½	.03½	.03½
Aluminium Sulfate (iron-free) . lb.	.02½	.02½	.02½
Ammonium Carbonate, pwd. . . lb.	.07	.07	.08
Chloride, white gran. . . . . . lb.	.07¾	.07¾	.07½
Ammonia, anhydrous . . . . lb.	.30	.30	.30
Ammonia Water, drums, 26° . . . lb.	.07½	.07½	.07½
Arsenic, white . . . . lb.	.07½	.08	.06½
Barium Chloride . . . . ton	*85.00	*85.00	*53.00
Nitrate . . . . lb.	*.06	*.06	*.07
Barytes, white . . . . ton	33.50	33.50	28.00
Bleaching Powd., 35%, works . . . . 100 lbs.	1.60	1.60	2.25
Borax, cryst., bbls. . . . . lb.	.05½	.05½	.05¾
Bromine, pure, wks. . . . . lb.	.25	.25	.23
Calcium Chloride, fused, f.o.b. N. Y. . . . . ton	24.50	24.50	28.75
Chlorine, liquid . . . . lb.	.06	.06	.06
Copper Sulfate . . . . 100 lbs.	7.00	7.00	5.55
Iodine, resublimed . . . . lb.	4.20	4.20	3.80
Lead Acetate, white crystals . . . lb.	.10½	.10½	.11
Nitrate . . . . lb.	.15	.15	.15
Red . . . . lb.	.08	.08	.08
White (Carb.) . . . . lb.	.07¼	.07¼	.07¼
Lime Acetate . . . . 100 lbs.	2.35	2.35	1.75
Magnesium Carbonate, tech. . . lb.	.06	.06	.06
Magnesite, calcined . . . . ton	55.00	55.00	55.00
Phosphorus, yellow . . . . lb.	*.25	*.25	*.27
Red . . . . lb.	*.26	*.26	*.30
Plaster of Paris . . . . bbl.	4.25	4.25	4.25
Potassium Bichromate . . . . lb.	.09¾	.09¾	.10½
Bromide, imported . . . . lb.	*.15	*.15	*.13
Carbonate, calc., 80–85% . lb.	*.04¾	*.04¾	*.04½
Chlorate, cryst. . . . . lb.	*.06½	*.06½	*.05½
Hydroxide, 88–92% . . . . . . lb.	*.05¾	*.05¾	*.06
Iodide, bulk . . . . lb.	3.30	3.30	2.90
Nitrate . . . . lb.	.08	.08	.08
Permanganate, U. S. P. . . . lb.	*.14	*.14	*.15
Prussiate, red . . . . lb.	*.90	*.90	*.29
Yellow . . . . lb.	*.32	*.33	*.24½
Salt Cake, bulk . . . . ton	21.00	21.00	17.00
Silver Nitrate . . . . oz.	.48	.48	.44½
Soda Ash, 58%, bags . . . . . 100 lbs.	*1.80	*1.80	*1.85
Caustic, 76%, N. Y. . 100 lbs.	3.60	3.60	3.80

*Resale or Imported (not an American makers' price).

	Aug. 1	Aug. 10	Jan. 1922
Sodium Acetate . . . . lb.	.05	.05	.04
Bicarbonate . . . . 100 lbs.	2.00	2.00	2.00
Bichromate . . . . lb.	.07	.07	.07¼
Bisulfite, powd. . . . . lb.	.04¼	.04¼	.04¼
Chlorate . . . . lb.	.06¾	.06¾	.07½
Cyanide, 96–98% . . . . lb.	.23	.23	.28
Fluoride, tech. . . . . lb.	.09½	.09½	.09½
Hyposulfite, bbls. . . . . 100 lbs.	3.25	3.25	3.50
Nitrate, 95% . . . . 100 lbs.	2.55	2.55	2.32½
Nitrite . . . . lb.	.09½	.09½	.06½
Prussiate, yellow . . . . lb.	.20½	.20½	.16½
Phosphate (di-sod.), tech . . lb.	.04	.04	.04¼
Silicate, 40° . . . . lb.	.01	.01	.01⅛
Sulfide, 60%, fused . . . . lb.	.04	.04	.05
Strontium Nitrate . . . . lb.	*.08	*.08	*.10
Sulfur, flowers . . . . 100 lbs.	3.00	3.00	2.75
Crude, mines . . . . long ton	14.00	14.00	16.00
Tin Bichloride, 50% sol'n . . . . . . lb.	.10½	.10½	.09¼
Oxide . . . . lb.	.38	.38	.37
Zinc Chloride, U. S. P. . . . . lb.	.35	.35	.35
Oxide, bbls. . . . . lb.	.08	.07	.08

ORGANIC CHEMICALS

	Aug. 1	Aug. 10	Jan. 1922
Acetanilide, U. S. P. bbls. . . . . . . lb.	*.29	*.29	*.29
Acid, Acetic, 28 p. c. . . . . . . 100 lbs.	2.67½	2.67½	2.37½
Glacial . . . . lb.	.11	.11	.10
Benzoic, U. S. P. . . . . lb.	.55	.55	.60
Carbolic, cryst., U. S. P., drs . . . . lb.	.15	.16	.12
50- to 110-lb. tins . . . . lb.	.21	.21	.18
Citric, crystals, kegs . . . . . . lb.	*.44½	*.44½	*.43
Oxalic, cryst., bbls., wks. . . lb.	.15½	.16	.14
Pyrogallic, resublimed . . . . lb.	1.60	1.60	1.75
Salicylic, U. S. P. . . . . lb.	.26	.29	.24
Tannic, U. S. P., bbls. . . . lb.	.70	.70	.75
Tartaric, cryst., U. S. P. . . lb.	*.28½	*.28	*.25
Acetone, drums . . . . lb.	.13½	.13½	.12
Alcohol, denatured, complete . gal.	.31	.31	.45
Ethyl, 190 proof, bbls. . . . gal.	4.65	4.65	4.75
Amyl Acetate . . . . gal.	1.90	1.90	2.00
Camphor, Jap, refined, cases . . . lb.	.80	.83	.90
Carbon Bisulfide, c/l . . . . lb.	.06	.06	.06½
Tetrachloride . . . . lb.	.10	.10	.10½
Chloroform, U. S. P., drums . . . lb.	.25	.25	.43
Creosote, U. S. P. . . . . lb.	.40	.40	.40
Cresol, U. S. P. . . . . lb.	.14	.14	.14
Dextrin, corn . . . . 100 lbs.	3.09	3.09	2.70
Imported Potato . . . . lb.	.09	.09	.06½
Ether, U. S. P., 100 lbs. . . . . lb.	.14	.14	.14
Formaldehyde, bbls. . . . . lb.	.08	.08	.10½
Glycerol, dynamite, drums . . . . lb.	.13½	.15	.14½
Methanol, pure, bbls. . . . . gal.	.72	.72	.75
Methylene Blue, med . . . . lb.	3.00	3.00	4.00
Petrolatum, light amber . . . . . . lb.	.04½	.04½	.05¼
Pyridine . . . . gal.	1.75	1.75	1.75
Starch, corn, pow'd . . . . . . 100 lbs.	2.47	2.47	2.13
Potato, Jap . . . . lb.	.07	.07	.06½
Sago . . . . lb.	.03½	.03½	.04



Courtesy of Drug & Chemical Markets

OILS, WAXES, ETC.

	Aug. 1	Aug. 10	Jan. 1922
Beeswax, pure white ... lb.	.40	.40	.33
Castor Oil, No. 3 ... lb.	.12	.12	.10½
Ceresin, yellow ... lb.	.08	.08	.07½
Corn Oil, crude, tanks, mills ... lb.	.09½	.09½	.06¾
Cottonseed Oil, crude, f. o. b. mill ... lb.	.08½	.08½	.07
Linseed Oil, raw, car lots ... gal.	.88	.88	.69
Menhaden Oil, crude, mills ... gal.	.43	.43	.35
Neat's-foot Oil, 20° ... lb.	.20	.20	.16¾
Paraffin, 128-130 m. p., ref. ... lb.	.03¾	.03¾	.05
Rosin, "F" grade, 280 lbs. ... bbl.	6.30	6.30	5.30
Rosin Oil, first run ... gal.	.39	.39	.36
Shellac, T. N. ... lb.	.78	.78	.66
Sperm Oil, bleached winter, 38° ... gal.	1.35	1.35	1.70
Stearic Acid, double pressed ... lb.	.09½	.09½	.09¾
Tallow Oil, acidless ... lb.	.10	.10	.10
Turpentine, spirits of ... gal.	1.18	1.18	.82½

METALS

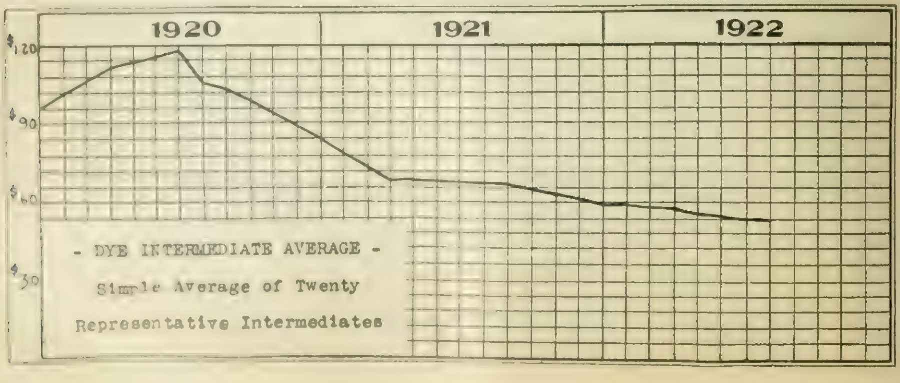
	Aug. 1	Aug. 10	Jan. 1922
Aluminium, No. 1, ingots ... lb.	.17½	.17½	.17
Antimony, ordinary ... 100 lbs.	5.25	5.25	4.55
Bismuth ... lb.	2.10	2.10	1.80
Copper, electrolytic ... lb.	.14	.14	.13⅞
Lake ... lb.	.14	.14	.13¾
Lead, N. Y. ... 100 lbs.	5.75	5.85	4.70
Nickel, electrolytic ... lb.	.39	.39	.45
Platinum, refined, soft ... oz.	93.00	93.00	78.00
Quicksilver, flask ... 75 lbs. ea.	55.00	57.00	52.00
Silver, foreign ... oz.	.71⅝	.71⅜	.65¼
Tin ... lb.	.32	.32	.32¾
Tungsten Wolframite ... per unit	2.00	2.00	2.00
Zinc, N. Y. ... 100 lbs.	6.25	6.60	5.20

FERTILIZER MATERIALS

	Aug. 1	Aug. 10	Jan. 1922
Ammonium Sulfate, expt. .100 lbs.	3.50	3.50	2.60
Blood, dried, f. o. b. N. Y. ... unit	4.00	4.00	3.50
Bone, 3 and 50, ground, raw ... ton	28.00	28.00	30.00
Calcium Cyanamide, unit of ammonia ...	2.75	2.75	2.25
Fish Scrap, dried, wks ... unit	4.10 & .10	4.10 & .10	3.25 & .10
Phosphate Rock, f. o. b. mine:			
Florida Pebble, 68% ... ton	3.00	3.00	5.00
Tennessee, 78–80% ... ton	4.00	4.00	8.00
Potassium Muriate, 80% ... unit	.60	.60	*.75
Tankage, high-grade, f. o. b. Chicago ... unit	4.00 & .10	4.00 & .10	3.00 & .10

COAL-TAR CHEMICALS

	Aug. 1	Aug. 10	Jan. 1922
Crudes			
Anthracene, 80–85% ... lb.	.75	.75	.75
Benzene, pure, tanks ... gal.	.30	.30	.29
Naphthalene, flake ... lb.	.06½	.06½	.07½
Phenol, drums ... lb.	.15	.15	.11
Crudes (*concluded*)			
Toluene, pure, tanks ... gal.	.30	.30	.30
Xylene, 2 deg. dist. range, tanks ... gal.	.45	.45	.45
Intermediates			
Acids:			
Anthranilic ... lb.	1.10	1.10	1.10
Benzoic, tech ... lb.	.50	.50	.50
Cleve's ... lb.	1.50	1.50	1.50
Gamma ... lb.	1.80	1.80	2.25
H ... lb.	.75	.75	1.00
Metanilic ... lb.	1.00	1.00	1.60
Monosulfonic F ... lb.	2.30	2.30	2.30
Naphthionic, crude ... lb.	.60	.60	.65
Nevile & Winther's ... lb.	1.20	1.20	1.30
Picric ... lb.	.20	.20	.25
Sulfanilic ... lb.	.22	.22	.26
Tobias' ... lb.	1.50	1.50	2.00
Aminoazobenzene ... lb.	1.15	1.15	1.15
Aniline Oil ... lb.	.14	.14	.17
Aniline Salt ... lb.	.20	.20	.25
Anthraquinone (sublimed) ... lb.	1.35	1.35	1.50
Benzaldehyde, tech ... lb.	.65	.65	.45
U. S. P. ... lb.	1.40	1.40	1.25
Benzidine Base ... lb.	.85	.85	.90
Benzidine Sulfate ... lb.	.70	.70	.70
Diaminophenol ... lb.	5.50	5.50	5.50
Dianisidine ... lb.	4.50	4.50	4.75
p-Dichlorobenzene ... lb.	.17	.17	.15
Diethylaniline ... lb.	.60	.60	.90
Dimethylaniline ... lb.	.32	.32	.40
Dinitrobenzene ... lb.	.20	.20	.21
Dinitrotoluene ... lb.	.20	.20	.25
Diphenylamine ... lb.	.58	.58	.58
G Salt ... lb.	.65	.65	.70
Hydroquinol ... lb.	.80	.80	1.35
Monochlorobenzene ... lb.	.10	.10	.10
Monoethylaniline ... lb.	1.00	1.00	1.00
b-Naphthol, dist ... lb.	.23	.22	.30
a-Naphthylamine ... lb.	.30	.30	.30
b-Naphthylamine ... lb.	.95	.95	1.05
m-Nitroaniline ... lb.	.72	.72	.85
p-Nitroaniline ... lb.	.75	.75	.77
Nitrobenzene (Oil Mirbane) ... lb.	.10	.10	.10
p-Nitrophenol ... lb.	.75	.75	.75
o-Nitrotoluene ... lb.	.12	.12	.15
p-Nitrotoluene ... lb.	.60	.60	.70
m-Phenylenediamine ... lb.	1.00	1.00	1.10
p-Phenylenediamine ... lb.	1.50	1.50	1.60
Phthalic Anhydride ... lb.	.35	.35	.38
R Salt ... lb.	.55	.50	.60
Resorcinol, tech ... lb.	1.30	1.30	1.50
U. S. P. ... lb.	1.75	1.75	2.00
Schaeffer's Salt ... lb.	.60	.60	.70
Sodium Naphthionate ... lb.	.60	.60	.70
Thiocarbanilide ... lb.	.35	.35	.40
Tolidine (base) ... lb.	1.15	1.15	1.20
Toluidine, mixed ... lb.	.30	.30	.30
o-Toluidine ... lb.	.16	.16	.20
p-Toluidine ... lb.	1.00	1.00	1.10
m-Toluylenediamine ... lb.	.95	.95	1.10
Xylidine ... lb.	.42	.42	.40



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EDITORIALS

Tariff without Protection

CONGRESS has just passed a tariff bill which makes the success of the chemical industry quite impossible. This action has been taken in spite of its avowed willingness to support our industry. The production of many synthetic organic chemicals in this country has been rendered as difficult as was the making of bricks without straw in the days of Pharaoh. The chemical industry has been left to the mercies of the "I. G." Potash developments are simply wiped out.

The first effect of the Tariff Act will be the possible failure, in increasing numbers, of the smaller concerns devoted to the production of greatly desired specialties. The total capitalization of 45 of them is about $30,000,000. The strongest of these concerns may be able to live long enough to develop new lines of production that will save something from the crash. Others may perhaps be taken into combinations, thus tending toward the very monopolies which we seek to avoid in America.

Another effect will be the discouragement of research and discovery. We wonder how many research organizations, perhaps on the verge of discoveries important to the human race, will disband in disgust and disappointment. Talent will be diverted from problems affecting public health and national defense, and the final results cannot but be seriously detrimental to the American people and to the economic future of America.

Allied lines will be adversely affected. Most of the money invested in these chemical plants has been paid for equipment. Producers of such raw materials as lime, salt, alcohol, sulfur, iron, and copper will all feel the effects.

The Tariff Act fails in that no consideration has been taken of present conditions abroad. The selective embargo for a short period would have enabled our industries to gain strength. With the return of normal conditions abroad they would have been in position to meet competition with very moderate tariff protection. This has all been lost in the present tariff. In its stead we have some products overprotected, some fully protected, but the great majority virtually unprotected. A chemical selling at fifteen cents carries a duty of sixteen cents, while articles selling for more than a dollar are less and less adequately protected, since they are subject to the same duty of sixty per cent ad valorem and seven cents a pound specific. This means that a great group of specialties cannot be produced in America.

Who is responsible for this condition of affairs? It is unfortunate that the chemical industry had to be in any way involved in politics. The chemical industry became something upon which to make political trades, and in the last hours of Congress the House and Senate engaged in the favorite government game of buck-passing. Those immediately responsible appear to be Senators Smoot, Moses, King, and LaFollette. It is hard to understand how Senator Smoot could battle, on the one hand for a high rate on sugar, when the interests he represents cannot hope to produce more than a fraction of the country's requirements, and yet work persistently from the start against an industry capable of producing eventually one hundred per cent of our country's needs. Senator Smoot is a powerful factor in Congress and from the start has fought the chemical industry. Why?

We are familiar with the tactics of Senator Moses and have our own opinions as to his motives. Senator King has been willing to carry out orders in the maneuvers and with Senator Moses threatened to filibuster against the whole bill if efforts were made to save the chemical industry. Senator LaFollette, besides supporting Senator Smoot in the Finance Committee, has been in reserve when needed.

Among the men who gave time and intelligent thought to the problem are Frelinghuysen, Wadsworth, McCumber, Watson, Sterling, McLean, McKinley, Townsend, Ransdell, Bursum, Broussard, Lenroot, and Curtis.

At the request of the Secretary of the Treasury a final effort was made to extend the embargo for at least ninety days, to enable customs officials to prepare for the administration of the Tariff Act. The Ways and Means Committee of the House reported favorably a resolution to this end, but the House refused to take it up until assured of favorable action by the Senate. On a point of order that such legislation must originate in the House, the Senate Finance Committee voted seven to five against reporting Senator Wadsworth's resolution, although some felt that the favorable action on the part of the House Committee satisfied the parliamentary point. With both houses of Congress reported willing to take the suggested action, the matter died on a parliamentary point urged by Senator Smoot.

Verily Congress chasteneth those whom it loveth!

The chemical industry fared much better at the hands of the Democratic party, and yet several Democratic senators, who had signified their intention to vote for the embargo, voted against it upon being urged by the Democratic leader, Senator Simmons, to do so because it had become Republican legislation. The Republican party was restored to power largely because of dissatisfaction with economic conditions. Many of the "best minds" in the Government, men who are supposed to bring their talents to bear on pressing economic and business conditions, have been silent and inactive. Of all government departments, the War Department alone has stood by the chemical industry and has shown some comprehension of what it means.

What can we expect in the affairs of state under such methods of government as now obtain?

We have learned that the one way to deal with politicians is at the polls. At the present time the whole country is interested in politics and the coming election. We chemists should make it our business to learn at once what those who hope to represent us think about the chemical industry and what they propose. Generalities will not suffice. We believe there are ways of interesting any individual in what chemistry means to him personally, and unfortunately in most cases the appeal will have to be to his personal interests. If we could elect a more aggressively sympathetic Congress as a result of the present situation, the price the chemical industry is asked to pay might not be too high.

While we fight at the polls with one hand, we must do the best we can with the other to carry on the chemical industry under the conditions imposed. We must show our good faith by creating our own standards of excellence. We must win the support of Americans for our products through unsurpassed quality and fair dealing. Even with greatly thinned industrial ranks we go forward, confident that a Congress can be elected which, profiting by the errors made during the session just closed, will do what is necessary to repair as much as possible of the damage.

If the calamity which we fear for the chemical industry does not materialize, it will be a miracle of the first magnitude, due to superhuman efforts of American ingenuity in the face of overwhelming odds.

Added Incentive

FROM TIME to time announcements are made of special grants of funds for particular problems, but this is the first time a science in America has been able to point to a great annual prize to be awarded the chemist residing in America who is judged to have accomplished the most for his chosen science and the world's welfare. The letter announcing the gift is given in full in this issue of the JOURNAL, among the transactions of the Council at Pittsburgh (p. 886).

The prize is yet to be given a suitable name, but it will undoubtedly be indicated in the rules governing its award, which will shortly be worked out by a committee to be appointed by President Smith (in conference with representatives of the corporation that is the donor). We venture to hope that this prize may be called the Nichols Prize, so named in honor of our past president, W. H. Nichols, to whose interest in chemistry and to whose special efforts we owe the establishment of this prize.

Obviously, no human effort is expended without an incentive of some kind. A few men are content to work toward the achievement of an ideal with no other object in mind. Many seek the truth for its own sake, and the fame which goes with discovery is frequently sufficient to urge men to unusual mental and physical effort. Much too often work is performed for monetary rewards only, and under such circumstances becomes routine in character and more or less unsatisfactory in performance.

In doing the everyday work of the world, most people are paid as they go. It is when fundamental things are accomplished, quite beyond the appreciation of the average man who barters and trades, that we turn to unusual honors and rewards to pay in some measure our debt of gratitude. Only in rare instances have scientists been repaid through the commercialization of their work; yet the race profits most if they continue in their laboratories unswerving from their original purposes. Important discoveries are seldom appreciated at the time except by the group within which the genius labors. The world needs a greater output of work of this character, and so far-sighted men have offered various incentives to induce men first to prepare for such a career, later to be confirmed in their desire to pursue fundamental work in pure and applied science, and occasionally have offered great prizes for the rare and outstanding achievements.

At another time we shall present a list as complete as possible of the studentships and fellowships established as incentives to train for greater things. There are many such opportunities for men to demonstrate more than average ability and many thousands of dollars are invested annually for this purpose.

A $25,000 prize for a chemist! Unrestricted as to the corner of chemistry in which he works, unlimited as to geographical location, free from the circumscriptions of time—just the ability and perseverance to do great things. Not only in 1923, but in each succeeding year this prize is to be awarded. We should like to see this prize won early in its history by some chemist who, although working more or less obscurely with meager equipment, in one of our smaller institutions, is nevertheless doing great things and serving as an inspiration to the man just entering industry.

What a splendid incentive has been added to those already existing for men to continue their attack upon chosen problems in the field of chemistry! What a great stimulation for American chemists to put forth the very best that is in them year after year! No one can prophesy the good that will come to the country and the race in future years because this prize has been established. An added incentive, it should inspire lofty visions of service through chemistry.

The Pittsburgh Meeting

THE PITTSBURGH Meeting was notable because of the large number of papers presented, the excellence of the program, the large attendance, and the successful management on the part of the local committees. We should fall far short of our duty if we did not express our gratitude to Acting-President Baker of the Carnegie Institute of Technology for placing at our disposal the dormitories and other buildings of his institution, and to Chancellor Bowen of the University of Pittsburgh for his cordial support.

The 453 papers presented before 17 divisions and sections speak eloquently for the productivity of American chemistry. Still, it brings forcibly before us a problem that has for a long time confronted us. The time has come when we must consider the desirability of establishing certain standards for meeting papers, and make it something of an honor to be allowed to present a paper. Such a standardization will tend to reduce the number of papers presented, thus affording more time for discussion. The importance of this action is emphasized by those of our number who have attended scientific meetings abroad, where—in marked contrast to American practice—learned discussion follows the presentation of practically every paper, adding immensely to its interest and value.

Too much cannot be said in praise of the Local Section for the splendid manner in which the entertainment features were conducted. The members were untiring in their efforts as hosts, and spared neither money nor time to contribute to our happiness and comfort. The industrial excursion on Friday was especially noteworthy.

Incidentally, chemists should take pride in the fact that a demonstration of the utility of chemical research illustrated with an internal combustion motor was permitted in Carnegie Hall, heretofore reserved for prima donnas and other artists.

We all came away from the Pittsburgh Meeting impressed with the fact that the chemical profession is looking up, and confident that the AMERICAN CHEMICAL SOCIETY is able to undertake and carry through whatever is worth while for chemists and chemistry.

Regulating Chemical Fire Hazards

CHEMISTS have often been accused of lacking proper interest in legislative matters, even when their own interests are vitally concerned. In no case has this been more forcibly illustrated than in the regulation of hazards incident to their own operations. A proper subject for municipal control, regulations along this line have been left largely in the hands of municipal fire departments throughout the country. In general, the guides by which such rules are drawn up have been little more than the personal experiences of the officials charged with this duty, aided in a general way by the rules of the Underwriters Laboratories. The result, as might be supposed, has been a miscellaneous collection of rules based on little more than an unwonted fear of anything of a chemical nature. In other words, a wholesale injustice has been done the industry without its having had a voice in the procedure.

A damaging fire in a warehouse situated in a thickly populated section of New York recently waked the fire prevention officials of the city to the dangers resulting from lack of logically framed laws. In conjunction with an association of warehousemen, the Bureau of Fire Prevention of the city has formed a committee to revise the regulations on the subject and welcomed the idea of having a representative of the

AMERICAN CHEMICAL SOCIETY sit with them in their deliberations. Following this suggestion, President Smith has appointed Dr. C. E. Munroe, chairman of the Explosives Committee, Division of Chemistry, National Research Council to represent the SOCIETY on this committee. Certainly no action more important to the industry as a whole could have been taken, and it is to be hoped that other municipalities will follow this admirable lead.

Recognition Won

THE FUTURE of the chemical industry is still somewhat uncertain, but we are optimistic as to the ultimate outcome, largely because of the recognition which has already been won for the science and the industry. There are, however, still too many men in public life who either fail to comprehend what chemistry means to America or who unhesitatingly put their personal interests before everything else. But a review of the discussions of chemical matters before both houses of Congress and congressional committees in the last few years cannot fail to convince us that our science has won recognition and that public men are beginning to acquaint themselves with creative, instructive, and productive chemistry.

The public press is finding in chemistry a subject of importance, both from the standpoint of news value and as a topic for editorial discussion. A notable example is an editorial on "Pandemic Chemistry" in the *New York Times* for September 11. After discussing certain features of the Pittsburgh Meeting, this editorial concludes:

> Every boy and girl and in time every man and woman should through school, newspaper, book, and magazine have this knowledge. If our high school students were to approach the science in this way, they would have a larger view than if they tried to grasp the complex problems of atomic structure and to fill their minds with the names of elements; then, too, more of them might be inspired to study it. The great chemical exposition to be held this week in the Grand Central Palace gives the public an opportunity to get some comprehension of what the vast range of this science now is. Such knowledge should become "pandemic."

Much remains to be done to make a knowledge of chemistry pandemic. The recognition already gained encourages chemists to greater efforts, and when the public knows about chemistry its encouragement will be demanded and its place in our economic fabric made secure.

An Appreciation of Fundamentals

WE ALL know that it is the seeking for truth for its own sake that gives us data upon which our material progress depends. But this view is seldom expressed in the lay press. "Uncle Dudley" brought out the plain facts clearly in an editorial in the *Boston Globe* for August 4, 1922, in which he defended the 19th century under the caption "Spare Those Bricks." We quote several paragraphs:

> We are prone to think of the 19th century as the one which gave us modern machinery; steam, electricity, flying and wireless. [illegible] product of something far nobler, and would that it had been, or were now, so regarded. It was a by-product of a fine and disinterested search for scientific truth.
>
> Scientific men disabused their minds of prejudice, religious bigotry, preconceived notions, narrow imaginings, and set forth to discover whatsoever of truth they could.
>
> The harvest was tremendous. And out of it came discoveries of general scientific principles which made possible the invention of this modern machinery which has become so much a part of our daily lives. But had these men of science set out with no higher aim than the invention of such machinery, that machinery never would have been invented. In order to do anything supremely well, one must be trying to do well the thing just next above it in difficulty and importance.
>
> In the early days of the Darwinian movement, Huxley, its lecturer-prophet, saw how things were likely to go and pronounced a solemn warning. He perceived that converts were flocking to his banner for the sake of the loaves and fishes, and cried out that if mankind regarded science and its discoveries not as a lofty and well-nigh religious quest of truth, but only as a means of padding their daily existences with material and bodily comforts, then it were better that these discoveries be not made than that humanity should use them as upholstery to an ignoble sloth.
>
> Huxley's worst fears appear to have been realized. The seizure of science to breed material wealth and heap up material comforts; the neglect of the fine spirit of truth-seeking, which alone gives science its fruitfulness, not to say its nobility, is exactly what happened. The 20th century was not 17 years old before every nation which had benefited by the discoveries of the 19th, was in a murderous struggle with and about the machinery of wealth-production; and science found itself conscripted to the task of human slaughter, which it performed with a thoroughness unexampled in history and which, if repeated, threatens to terminate history and civilization.
>
> The 19th century has been blamed for sowing the seeds of the World War. As well blame your parents for your combative instinct.
>
> We inherited two things from the 19th century. One was the example of a disinterested search for truth which made the Darwinian age an age of triumphs and secrets wrung from nature's close reserve. The other was the machinery which those discoveries made possible. The machinery, the material wealth, and the bodily comforts it has provided, we of the 20th century have grabbed, gobbled, used and abused. The results have been frightful beyond anything in recorded history. The lofty and dispassionate search for truth we have neglected. That was what made the 19th century great. It is the only thing that can make any century great. Until we apply it to the social quandaries created by this new machinery, our own century will have no greatness, nor anything but squalor.

Quackery to Walk Plank

FOR SOME years leaders in the American Medical Association have desired means for so educating the intelligent laity that quackery, from which we still suffer greatly, could find no fertile soil in which to flourish. The news service of the Association accomplished a great deal and yet was not just what was needed. Before the Great War it was decided to launch a journal to popularize medical information, but war work interfered.

Now that the printing plant is being greatly enlarged, the journal is to be undertaken under the initial guidance of Dr. V. C. Vaughan, who has been a leading spirit in the plan for years. People are to be told in an interesting way about public health, prevention of disease and curative medicine—all authoritatively. Misinformation will be shown up and we see dark days ahead for the quacks.

In chemistry we have also talked for years about a popular journal managed by our SOCIETY. The need and the opportunity still exist, and the difficulty is largely one of funds. The *Journal of the American Medical Association*, with a circulation nearing 100,000, earns a large sum annually and supports many worthy activities. With adequate support the publications of the AMERICAN CHEMICAL SOCIETY can also be developed into properties capable of earning a large part of the funds desired, not only for a popular journal of chemistry but for other worth-while projects. And we believe that to fill its mission properly a journal of popular chemistry must be managed by the AMERICAN CHEMICAL SOCIETY. Quacking wherever it exists must be made to walk the plank. Education is the best weapon and must be greatly extended. It is the education of our masses that constitutes our best defense against quackery, whether it be in economics, religion, science, or government.

PITTSBURGH MEETING AMERICAN CHEMICAL SOCIETY

The meeting was well attended approximately 15,000 being present. The Pacific Coast, the Atlantic Coast, the Gulf Coast, and Canada, each sent a goodly number, which, when added to the number from intermediate points, constrained one to wonder at the persistent talk of hard times and railroad strikes. Evidently, expense accounts retain some of the flexibility of former days, and the seriousness of the railroad situation had been largely overcome except in the newspapers. The presence in the Mississippi delegation of the chemical family of Swan, consisting of a father and four sons, set a record for families of chemists. The delegation from the University of Washington was large enough to justify a meeting of its own, although the Pacific Coast delegation as a whole did not succeed in getting the meeting next fall for San Francisco. Milwaukee persuaded the Council to take the meeting there instead.

The General Meetings on Tuesday and the reception on Wednesday were all that could be desired. The excellent papers given at these meetings may be read on pages 887 to 905 of this issue. Our President's address, "Our Science," was enjoyed by the public as well as by the members of the SOCIETY.

Automobiles and the possibility of smoothing out the operation of the family flivver to compare with that of "high brow" cars by the judicious use of diethyl selenide or tetraethyl lead, received a just share of attention, following the paper and experiments by Midgley and Boyd at the General Meeting. While the authors admitted that great good might be accomplished in removing detonation knocks by their method, they were unwilling to admit that they had found a cure-all for automobile ills, and stated that the regular service stations would have to be called in almost as usual.

Then the smoker! The more said the better, for certainly it was a genuine success. "Section Q" must have rolled violently in its grave with jealousy that Syria Mosque should have housed an event so reminiscent. Several of the large industrial laboratories in the Pittsburgh district staged individual skits that were well calculated to arouse the envy of the vaudeville kings. The general title applied by the perpetrators was "H_2O," and there was nothing dry about it from the first entrance of Dr. Halogen, of Freshwater College, to the final exit of the beautiful Miss Oxy Gen, vivid vamp and sister to Hydro, the volatile virgin. Movies of the activities of the Pittsburgh Section, shown for the benefit of sectional chairmen and secretaries, included many valuable suggestions for keeping up interest. Then the chef of the mosque spread himself for the profound benefit of all. One of the most attractive features of the smoker was the program, which included songs (to popular airs) written especially for the occasion.

Wednesday and Thursday were profitably spent in divisional meetings and symposiums at the Carnegie Institute of Technology. Each Division was well attended and interest in the various papers ran high. The arrangements for caring for interdivisional visiting were well handled, including bulletins on the campus as well as in each divisional meeting room, which showed at all times the papers being read and those next expected.

The meeting of the Metric System Committee with representatives of twenty other scientific societies to consider ways and means of forwarding the general adoption of the metric system in this country, was one of the features of Wednesday afternoon. The question of educating the general public to the advantages of the system was considered, and a resolution adopted to request the Bureau of Education in Washington to use such means as it might command to increase the more thorough teaching of the metric system in all schools. The meeting favored the double marking of goods with both the metric and avoirdupois quantities, as a means of gradually educating the public to the general use of the former. However, the general sense of the meeting was that the change from one to the other would best be accomplished by gradual educative means rather than by any radical step. Reports from the various organizations indicated that in every case except those of the civil engineers, architects, and electrical engineers, progress was being made in introducing the system into general use in the industry represented. The following organizations were represented at this meeting:

American Chemical Society, Eugene C. Bingham, *Chairman*
American Psychological Association, W. V. Bingham, *Secretary*
National Academy of Sciences, W. A. Noyes for T. C. Mendenhall
American Institute of Electrical Engineers, N. W. Storer for Charles E. Skinner
American Metric Association, W. W. Stevenson
Optical Society of America, Harry S. Hower
U. S. Bureau of Standards, F. S. Holbrook
American Statistical Association, Roswell H. Johnson
Geological Society of America, Roswell H. Johnson
American Electrochemical Society, R. E. Zimmerman
American Pharmaceutical Association, J. A. Koch
American Astronomical Society, Herman S. Davis
Maryland Academy of Sciences, Claude H. Hall
American Association of University Professors, A. Silverman for Carl D. Schwartzel
American Institute of Architects, T. E. Billquist
American Society of Civil Engineers, R. A. Cummings
American Medical Association, Paul N. Leech
Mathematical Association of America, Dr. Bishop
American Physiological Society, C. C. Guthrie
American Public Health Association, A. B. Wadsworth
Illuminating Engineering Society, E. J. Edwards

Friday's excursion to the plants of the Carnegie Steel Corporation and the American Window Glass Company was greatly appreciated by the more than 400 who attended. The smoothness attending all arrangements was certainly a credit to those in charge. The structural steel process was followed from the ore to the finished steel, and the immense by-product coking plant which furnished the fuel for the steel manufacture was inspected. Lunch was served by the Carnegie Steel Corporation in the giant air-compressor plant, and the party was taken on to the glass plant to inspect its complete cycle of operations from the raw material to the finished sheets. Saturday's excursions to various plants in the district were less well attended, but none the less interesting.

Beginning with the advent of the two woman councilors, Misses Pennington and Woodford of New York, the ladies were well represented at all the gatherings. Entertainment especially for the ladies consisted of theater parties, a drive to the Pittsburgh Field Club, an excursion to the factory of the H. J. Heinz Co., inspection of the library, museum, and art galleries of the Carnegie Institute, a lecture by Homer St. Gaudens, a most attractive garden party, buffet supper, and dance at Oak Manor (to which all were invited), a drive to the Allegheny Country Club, and a farewell reception and musicale at the 20th Century Club.

The entire Pittsburgh Section, and especially those responsible for the various entertainments, provided a meeting which will be long remembered as one of the outstanding events in the history of the SOCIETY.

Council Meeting

The meeting, with an attendance of 120, began its work in excellent spirits, following the announcement by President Smith that a prize, as yet unnamed, but comparable to the Nobel prize in value and importance, has been provided for American chemistry. He read the following letter, which he had received from the Allied Chemical and Dye Corporation:

> AUGUST 30, 1922
>
> MY DEAR DR. SMITH:
>
> [illegible] yesterday, it gives me great pleasure to state that the Allied Chemical and Dye Corporation desires to institute an annual prize of $25,000 to reward the chemist, residing in the United States, who in the opinion of a properly constituted jury has contributed most to the benefit of the science and of the world. Realizing, as we do, the enormous influence which chemists working in all the fields of that science will have on the welfare of the world, we desire by this prize to so encourage the workers that even larger benefits should accrue than those which have already placed the world under such a debt of gratitude to the profession.
>
> We desire that you shall make this announcement at such time and place as you shall deem best, and to take such steps as may be necessary to carry the matter into effect beginning with the year 1923. We assume that a committee, of which you will be chairman, will be appointed by you to consider and suggest the rules governing the selection each year of the chemist who is deemed most worthy.
>
> We also assume that this committee will provide for the appointment of a jury to decide annually who should be the recipient. We would be glad if the committee would arrange the selection of this jury so that this Company would have the appointment of two members, it being understood that neither of those members should be connected with the Company.
>
> We do not desire to limit the gift to any particular field of chemistry, recognizing as we do the importance of them all.
>
> As the American Chemical Society is by far the largest organization of chemists, and represents every field of the science in its membership, we have thought it better to work through that Society, although not limiting the gift to its members. Our sole desire is to encourage chemists everywhere in our country to do even more than they have been doing for the [illegible]
>
> We have not gone into details, as we value greatly the opinions of those who would naturally be asked to serve on the committee, and do not desire to trammel them in their deliberations.
>
> Yours very truly,
>
> (Signed) WM. H. NICHOLS, *Chairman*

The announcement was received with great applause and the President appointed a committee to prepare appropriate resolutions accepting the gift.

The by-laws of the Cellulose Division were accepted, and those of the Petroleum Section referred back to the Section, for discussion and presentation to the Advisory Committee at a later day. The by-laws as resubmitted were approved later in the week by the Advisory Committee.

Milwaukee was chosen for the autumn meeting of 1923, which will be held during the week beginning Monday, September 10.

[illegible] the [illegible] Society will coöperate, has determined to join with the American [illegible] of the *Journal of Physical Chemistry*. [illegible] were presented and a motion to approve the action taken and the [illegible] A [illegible] passed in which the Council expressed the hope that the new Board of Editors [illegible] of the Journal of the American Chemical Society, of the Chemical Society (London) and of the Faraday Society, in order to prevent unnecessary overlapping of the fields covered in their respective publications.

A. B. Lamb was reëlected Editor of the *Journal of the American Chemical Society*, E. J. Crane of *Chemical Abstracts*, H. E. Howe of *The Journal of Industrial and Engineering Chemistry*, and W. A. Noyes of *Scientific Monographs*. The selection of associate editors for the *Journal of the American Chemical Society* and for *The Journal of Industrial and Engineering Chemistry* was left to the editors, their nominations to be approved by the Directors. John Johnston's report on *Technologic Monographs* was presented, followed by his resignation, effective December 31, 1922. The Council empowered the Advisory Committee to select his successor, and a vote of thanks was passed expressing appreciation for the admirable work which Dr. Johnston has done. Charles L. Parsons was unanimously elected Secretary of the SOCIETY, and an *ad interim* report of the Treasurer was presented showing that the SOCIETY, because of reduced costs and careful management, is keeping within its income.

The Advisory Committee was then empowered to select four members to represent the AMERICAN CHEMICAL SOCIETY on the Board of Editors of the *Journal of Physical Chemistry*, and suggestions were invited from members of the Council.

The motion to increase the allotments of Local Sections was again laid upon the table, to be considered anew at the Milwaukee meeting.

The Cornell Section presented an invitation to the SOCIETY to meet in Ithaca in 1924, which was filed for attention one year hence.

After discussion it was voted that no change be made in the policy toward student members, and that they should continue to receive the advantages of the $10 rate so long as they are *bona fide* students majoring in chemistry in colleges and universities. The following motion was adopted with reference to the presentation of papers by nonmembers:

> On recommendation of the Advisory Committee, it was voted that, owing to the large number of papers being offered by the AMERICAN CHEMICAL SOCIETY, it is a ruling of the Council that papers by nonmembers may be placed on the program only when of unusual importance, and then only with the joint approval of the Secretary of the Division and the Secretary of the SOCIETY.

A committee was appointed to consider the importation of scientific books at reasonable rates, and instructions adopted calling upon our Committee on Nomenclature to use its best efforts to bring about a more general use of approved chemical spelling and nomenclature by all concerned.

In discussing the various fellowships and studentships supported by industry, the Editor of *The Journal of Industrial and Engineering Chemistry* was instructed to do what he could toward securing a complete list for publication in THIS JOURNAL.

The following resolutions submitted by the Advisory Committee were unanimously adopted:

> The AMERICAN CHEMICAL SOCIETY, representing every phase of pure and applied chemistry, in annual meeting desires to express its appreciation of those men in public life, who, notwithstanding the multitudinous demands upon their time, have been willing to endeavor to inform themselves regarding chemistry and its relations to public welfare, national defense, and industrial progress.
>
> They are also to be commended for the manner in which they have declared their findings and the action which they have been willing to take toward securing results believed to be beneficial to our country.
>
> The AMERICAN CHEMICAL SOCIETY further expresses its thanks to Francis P. Garvan, president of the Chemical Foundation, for his sincere efforts to secure for America a well-rounded chemical

industry, for his assistance in the education of the public to the importance of chemistry, and for his aid in fostering research and the publication of its results.

A. V. H. Mory gave a brief outline of the work of his committee on reorganization, indicated something of the scope which they intended to cover, answered certain questions with respect to the points under consideration, and expressed the hope that a constructive report might be presented at the New Haven meeting.

The concluding business of the meeting centered about the report of the Committee to consider the question of a non-society employment bureau, of which Charles L. Reese is chairman. The Committee recommended greater activity on the part of Local Sections and other groups in a position to aid men locally, and in assisting those employing chemists to secure men well qualified for the particular place. This portion of the report was adopted, and followed by a motion calling for a consideration by the Committee after consultation with the Secretary of the SOCIETY and the Editor of *The Journal of Industrial and Engineering Chemistry*, of a plan to inaugurate in the office of the Secretary or the Editor of *The Journal of Industrial and Engineering Chemistry* a clearing-house for the exchange of information between Sections and other groups relative to any excess of either men or positions in various localities. A tentative budget based on this plan is to be presented at the Directors' meeting in December.

The Council adjourned with suitable motions expressing appreciation to all those who participated in making the Pittsburgh meeting so successful.

The Human Side of Chemistry

By Edwin E. Slosson

SCIENCE SERVICE, 1115 CONNECTICUT AVE., WASHINGTON, D. C.

A HUNDRED years ago chemistry was a toy. To-day it is a tool. From the diversion of the philosopher it has developed into a practical profession of the highest importance to humanity. All the sciences may be expected likewise to earn their own living when they get old enough. But chemistry has in an astonishingly short time reached maturity and become more than self-supporting. We have recently seen factories hatching from test tubes, like fowls from eggs. Some of our friends in sciences that are older but do not yet pay dividends look upon chemistry with a certain suspicion and perhaps envy because of its success in a business way. They want to keep science as a sport and seem anxious lest the chemist lose his amateur status by making money. They need not worry, for whatever rewards come to the chemist—or to his employer—will be an infinitesimal fraction of what chemistry has given to the world.

E. E. SLOSSON

THE CHEMIST TOO MODEST

The chemist is the most modest of men. He does not claim credit for what others do. He does not claim credit for all he does. Indeed, he often disclaims credit for some of his highest achievements. If he makes butter, he is willing that the credit should go to the cow, while he takes the cash; if he spins the silk for a dress he pretends that he is a mere worm; if he constructs a pearl he disguises himself as an oyster. He will even condescend to take the place of the humble tortoise and secrete a shell.

Modesty is an admirable thing, but it has its dangers if overdone. When you assume a deprecatory attitude toward your achievements, there is always the danger that other folks may believe you. They may take you at your own pricemark. It is safe to profess unworthiness only when you are sure that those present will contradict you.

The result of this persistent attempt of the chemist to minimize his own importance is that the outside world fails to appreciate the value of his contributions to modern civilization and does not at all realize what the chemist might do in the future if he had a free hand. Don't camouflage your creations by calling them imitations. If you invent a synthetic plastic, some condensation product of phenol with an aldehyde or an amine, don't call it a mineral or vegetable. Name it after yourself.

A synthetic product should have a synthetic name. One of the fortunate effects of the unfortunate failure of our patent laws to afford proper protection is that it has led to the coining of new names for new things; too often to the coining of new names for old things, it is true, but still a good movement, for it brings people to the recognition of the fact that there are new things under the sun and that most of them come from the chemist. The chemist has become the greatest coiner of words in the world. The rapid expansion of organic chemistry demanded the fabrication of some 250,000 new names, with provision for an indefinite increase in the future. Nobody ever had such a job since Adam was called upon to give names to all the animals as they filed before him. It meant doubling the dictionary. In accomplishing the gigantic task of constructive philology, the chemist has got some unwieldy combinations, but on the other hand he has under the pressure of commercialism contrived some very neat and handy nicknames for everyday use. The coinage of "Kodak" confounds the philologists. But they have determined the derivation of "balopticon" to their own satisfaction. It is derived, they say, from two Greek roots "ballo," to throw, and "optikos," sight, a very proper term for a projection lantern, and removes the suspicion that the name of the apparatus might conceal a sly reference to its makers, the Bausch & Lomb Optical Company.

This is much better than the old custom of carrying over old names to new things. Fish glue films were called isinglass as though they were a kind of glass. When mica took its place it too was called isinglass, even in stove windows, and what is now called mica is mostly celluloid, and what is called celluloid, may be something else. Language lingers and lags behind the advance of science. That is because the public cannot realize the creative power of chemistry—that a compound is a different thing from the elements that compose it.

New Era in Chemistry

In chemistry the whole is not equal to the sum of its parts, never qualitatively and possibly not always quantitatively. If we put together four atoms of hydrogen each weighing 1.008 we get one atom of helium that weighs only 4. The .008's have somehow got lost in the shuffle.

Chemistry is the creative science. Don't suspect me of taking advantage of my position to work in anything personal. I am quoting Berthelot, who foretold the time when all our foods would be made by the chemist. I do not see so far ahead as that, but it is certain that chemistry is entering upon a new era when its constructive powers will have wider scope and largely relieve us of our forms of life. The chemist of the future will not be content to do analytical work such as the house wrecker does, or imitative work such as the forger does, but the chemist will do original work such as he alone can do.

The future of civilization is fixed by the scientist because he has the power to control the basic reaction on which our vital and mechanical power depends, the oxidation of carbon and hydrogen. All wealth is in its essence energy, and the material sources of energy are practically but two, food and fuel, very similar in composition and just alike in their final products. If the fuel falls short, our modern civilization will disappear and humanity will revert to a primitive condition. If our food supply falls short, life itself will be limited. The two factors of civilization, mass and potential, population and the standard of living, quantity and quality, are functions of the food and fuel supply. The Law of Malthus has often been refuted but has never been repealed. The world has now been all surveyed and staked out in claims like a mining camp after the first rush is over. Quarrels over stakes and limits will continue and we can only hope that they will be settled in court rather than by the cruder methods of Roaring Camp. The late unpleasantness was started by a claim jumper who was too quick with his shooting iron and had to be handled by the vigilance committee. But how such quarrels are to be settled in the future is no more the concern of the chemist than of any other citizen. The peculiar business of the chemist is to see that there is something worth quarreling about. He is to show how to create and economize wealth and is not responsible for its abuse and destruction.

The period of the extension of civilization is approaching its end, and henceforth progress must take the form of intensification of civilization. People must cease to expand and begin to construct. There are no more continents to discover. No more worlds to conquer. The new era will require new methods and here the constructive powers of the chemist will come into play. The world will more and more come to depend upon him. It does not require any chemistry to pick a cocoanut off a palm tree. It only requires a rope and prehensile toes. But it does require chemistry to extract the oil from the copra and hydrogenate it and sell it as a bread spread to a hostile public. It does not require any chemistry to manure a field, but it does require chemistry to fix the free nitrogen of the air.

Chemistry is continually gaining ground from biology. Vast areas, which biologists once claimed but had neglected, have now gone over to the chemists. In fact, it seems that whenever a vital process or product had been thoroughly studied and understood, it is found to belong to physics or chemistry. Consequently, the chemist is inclined to regard biology as merely an unexplored province of chemistry. Many a loyal biologist in pursuit of some legitimate line of research well within his own territory has found in the course of time that he has unconsciously become a chemist. Pasteur many years ago crossed the boundary in the opposite direction; while hunting up assymmetric crystals he got over into abiogenesis. As an offset to our gains from biology we have lost to physics the invaluable province lying inside the atom. In the *modus vivendi* that prevailed when I was a student, anything bigger than the molecule belonged to the physicist, and everything smaller to the chemist. But a band of bold physicists, led by Thomson and Rutherford, made a raid into the hinterland of chemistry and captured the interior of the atom. Scientific boundaries, like national boundaries, are merely imaginary lines and may be drawn at convenience, though they are mostly drawn at inconvenience.

The new era that we are entering is a period of merger in the sciences. The traditional boundaries are being wiped out. The nice precise little dogmatic definitions and distinctions that used to fill the first few pages of an elementary chemistry textbook have run together like bad dyes in warm water. The old arbitrary division lines between chemistry and physics, organic and inorganic, natural and artificial matter and energy, molecule and mass, chemical affinity and adhesive forces, are disappearing. Scientists are discovering what the artists have long known—that there are no lines in nature.

Acetic acid may be made by a vinegar plant *or* by a hydroelectric plant. A reaction may be accelerated by a high temperature *or* a catalytic metal. It has recently been announced that rickets in children may be cured by sunlight *or* cod-liver oil. Let us hope that the children will be allowed their choice of which remedy they will take.

Every annual session of this Society knocks some of our old ideas in the head. At this meeting Professor McKee will try to persuade us that there is no shale oil in oil shale, and Professor Bancroft that there is no color in the peacock's tail.

Chemistry is now passing through a revolutionary era like that of 150 years ago when Lavoisier's balance overthrew the phlogiston theory. But as Priestley stuck to phlogiston to the day of his death, although his discovery of oxygen had given it the deathblow, so some of us elders show a certain reluctance in relinquishing our old familiar images. There was something solid and satisfying about our molecular models made of wooden balls, stained with aniline dyes and stuck together with wires. But these have now been relegated to the top shelves of the storeroom and we have to get used to a newfangled atom, composed of a vacuum and algebraic symbols. Minus marks are flying round a plus mark like automobiles on a race course and whenever one skids it flashes its light. In place of a stout wirey valence bond, stiff and straight, that sticks when it is once put into its hole, we are offered two electrons playing tag in a ring, like cats chasing each other's tails.

But the new conceptions, as we all realize, are vastly in advance of the old, for they give us the ability to handle the ultimate and individual units of matter. Clerk Maxwell held that the laws of nature were merely and inevitably statistical, that we could only deal with averages of multitudes of indistinguishable molecules and movements. If that were true, chemistry would be less of an exact science than sociology, for the chemist cannot tell within many million how many molecules will pass in a minute through a tube connecting two flasks of gases of unequal density, while the social statistician can tell within a few thousand how many people will pass in a day through the Hudson tube connecting Jersey City and New York. But now that we have the power to discern and track the individual atom and even electron, Maxwell's argument no longer holds. We can sort out isotopes by their weights and divide electrons according to their velocities. We have, therefore, virtually found the sorting demon which, as Maxwell foresaw, might upset or evade the second Law of Thermodynamics and so bring order out of disorder and work out of uniform temperature.

Maxwell argues that all the atoms of an element must have the same weight, for he says ("Theory of Heat," p. 329):

> If the molecules of some substance, such as hydrogen, were of sensibly greater mass than others, we would have the means of producing a separation between molecules of different masses and in this way we should be able to produce two kinds of hydrogen, one of which would be somewhat denser than the other. As this cannot be done, we must admit that the equality which we assert to exist between the molecules of hydrogen applies to each individual molecule and not merely to the average of groups of millions of molecules.

But now that Harkins has been able to separate hydrochloric acid gas into denser and rarer portions by simply passing it through a series of church-warden tobacco pipes, Maxwell's argument proves the reverse of what he thought.

Energy, like matter, has come under the atomic theory, and here, too, we are becoming acquainted with its individual units. As Millikan catches and counts the electrons on suspended droplets, so Silberstein catches and counts the quanta of light on Trivelli's silver bromide crystals. A single quantum of light knocks out an electron from a molecule and so disturbs the equilibrium of the salt that the whole crystal can be reduced to the metallic state by a developer. A faint light hits only a comparatively few crystals here and there upon the sensitive plate. A longer exposure hits some more. So Silberstein concludes that light comes like scattered raindrops, not in a continuous stream. I gather from this that we should not speak of "a flood of light," for according to Silberstein it never pours but it rains.

Possibly these wavy arrows of actinic rays, which knock off electrons so easily when they hit a metallic target, may instigate in the same way other or all reactions started by light. This may be the signal that starts the machinery going in the carbohydrate factory of the green leaf. If so, we may learn to better nature in this business as we have in others and set up solar engines of our own.

The chemist provides the motive power of the world, the world of man, not the inanimate globe. Archimedes said he could move the world if he had a long enough lever. The chemist moves the world with molecules. If he can only get control of the electron, he will be in command of unlimited energy. For in this universe of ours power seems to be in inverse ratio to size and the minutest things are mightiest.

When we enter the realm of intra-atomic chemistry, we get behind the elements and may effect more marvelous transformations than ever. The smaller the building blocks the greater the variety of buildings that can be constructed. The chemistry of the past was a kind of cooking. The chemistry of the future will be more like astronomy; but it will be a new and more useful sort of astronomy such as an astronomer might employ if he had the power to rearrange the solar system by annexing a new planet from some other system or expediting the condensation of a nebula a thousand times.

But if the chemist is to become an electron astronomer, he will have to become a mathematician of the highest order. He may even have to enter the fourth dimension. In the good old days a chemist did not have to know any mathematics but arithmetic and that only as far as percentage and the rule of three. He had nothing harder to do than to figure out his analyses so as to add up to 100 per cent, and he did not dare to bring them out exactly to 100 because that would look suspicious. But some twenty years ago it became apparent that the chemist could not keep up with the progress of his science unless he passed in mathematics beyond the eighth grade. It was then that I dropped out of chemistry and took to journalism, a field that so far has not been invaded by the mathematician.

The constructive chemist must often begin by destruction. He must shatter this sorry scheme of things in order to remold it nearer to his heart's desire. To effect the disintegration that must precede the reintegration, the most useful agencies are high temperature and pressure.

THE FUEL PROBLEM

The strike has brought home to us the fuel question—since it does not bring home the fuel. The expansion of population and the development of civilization, even their maintenance at the present standard of life, depend upon finding new and perpetual sources of mechanical energy. The paramount importance of this question has been recognized by the International Research Council, which at its Brussels' meeting on July 25 adopted, as one of three subjects for coöperative study by the twenty nations represented, the investigation of the energy supply of the world. This was a project recommended by the National Research Council of the United States, which presented a plan for the systematic survey of all possible and conceivable means of obtaining mechanical power for the purpose of ascertaining which seem sufficiently adequate and feasible to warrant special research. In this international investigation of the dynamic foundations and future of our civilization, the AMERICAN CHEMICAL SOCIETY is qualified to take a leading part. No achievements would be better worth our $25,000 prize than a discovery opening up a new source of mechanical energy.

All our food and all our fuel, all our muscular and machine power, depend upon the peculiar ability of the little green granules of vegetation to build up carbohydrates out of air and water. The green leaf reaction—or, if you insist upon having it in Greek, the chlorophyl reaction—is the sole support of all plant and vegetable life and without it the earth would be a desert planet like the moon.

If the work of the world were really done by "horse power," as we still call it, man would have reached the limits of civilization a hundred years ago, for a horse requires hay and hay requires land and there would not be enough land in the world to provide for the horse power we are now using. Supplementing the green fields with the coal fields, man has not only prevented civilization from coming to a stop, but has given it an unprecedented forward impetus. The iron horse feeds on subterranean pastures. He is living on crops of the Carboniferous Era. Modern civilization basks in the sunshine that fell upon the earth unmeasured millenia ago. We are living on our capital, drawing on the coal banks. Sometime we must begin to earn our own living, to grow our fuel as we go.

Meantime, the amount of solar energy that is being stored up in the plants every summer is ten times as great as that released by the combustion of coal. But coal is more condensed and convenient than wood. Oil and gas are still better fuels. It would seriously check the progress of civilization if the world had to return to the wood basis, as it was 150 years ago.

We have been wasting year by year half of our natural gas and three-quarters of our petroleum. The supply of gas has fallen off by a quarter in the last five years, and soon will be running short. Our oil reserves will not last long, fifteen or twenty years at the present rate of consumption is all the geologists will allow us. At any rate the gasoline tank is getting low and no service station is in sight.

Still the trees and tiny plants flaunt their foliage provocatively in the face of the passing scientist, who must confess that he can not yet accomplish what they do so easily—these little green-leaf laboratories, these filmy factories, noiseless, smokeless, odorless, that with no reagents but air and water and no power but the sunshine build up by the ton the most complicated carbohydrates out of the simplest compounds of the commonest elements, carbon, hydrogen and oxygen.

Still, the sun, sole source of all our life and weather, floods half the earth with its rays, and the land that receives the most of this potential wealth is the land that retains the least of it, the arid region of the tropics. A section of the Sahara, forty miles square, receives in six hours a day as much heat as is produced by the coal burned in the twenty-four hours throughout the world. If only a small fraction of this wasted energy could be

economically stored up and set at work by some sort of solar engine, we need not worry about the exhaustion of our oil, gas, and coal. There would be wealth enough for all.

Here, then, is the greatest problem of conservation, the kind of conservation that consists in utilization. But, being accustomed to such wastefulness, it does not excite attention. Nobody is bothering about it except a few chemists, and they do not know how to help it.

Every tiny grass blade points the finger of scorn at the chemist and says "See how we do it. Don't you wish you could?"

And the chemist, with command of pressures varying from a vacuum to the point where steel flows like tar, and with command of temperatures ranging from the boiling point of carbon almost to absolute zero, is still obliged to confess that he cannot accomplish on a commercial scale the simple reaction of the polymerizing of formaldehyde. Even if he knew how, he could not hope to compete with plants on their own ground because they have at their command free raw materials and the cheap labor of protoplasm. Even a professor of chemistry cannot live as cheaply as a cornstalk.

But there are as many celluloses as there are sugars and it is not probable that those that the plants have prepared for their own purposes would be the best for all human purposes. Just as we have found that better dyes and drugs can be made in the factory than can be found in nature, so we may surmise that some of the fundamental foodstuffs—starches, sugars, fats, and even proteins—may possibly be improved upon.

More important and promising than the possibility of synthetic food is the possibility that we may devise some better method of capturing solar energy than the plants have hit upon. We have no reason to assume that the carbohydrates are the only way of solidifying sunshine. The chlorophyl process is shockingly wasteful. Less than one per cent of the solar energy that falls upon a leaf is fixed in the form of carbohydrates, from which it may be later released by oxidation. The crude steam engines, set up in Egypt, catching sunshine by cylindrical mirrors and throwing the heat upon blackened water pipes, have an efficiency of some four per cent, much higher than the green plant.

But a steam engine at best is an inefficient machine, and now that we are able to guide streams of electrons where we will and sort them out according to speeds by means of grids acting like Maxwell's demon, we may reasonably hope to utilize the radiant energy of the sun directly for power purposes. This is not a visionary project such as drawing upon the exhaustless forces inside the atom. That may, for all we know, remain forever an impossibility. What I am talking about, the fixation of solar energy, is something that we know can be done, for we see it in the grass every sunny day. If sunshine can excite a selenium cell and decompose silver bromide on a photographic plate, it may be made to do work of another sort and on a larger scale. Here, at any rate, is the greatest problem that the world presents, and the highest prizes are offered for its successful solution.

"EXPERIMENTS OF LIGHT"

I suppose that all of us have tried erratic experiments that we would not care to confess before our colleagues in such an assemblage as this. Crazy ideas will pop up in the best-regulated brains from some subconscious cellar, and we try them out on Saturday afternoon when there is nobody else around, just to see what will come of them. They do not appear in our published reports—unless they happen to succeed—in which case we claim full credit for our foresight in undertaking an operation that ordinary minds would have condemned in advance as absurd.

Now it is interesting to observe that such irrational experimentation is distinctly recommended by the philosopher who laid down the laws of experimental science that have in the three centuries since accomplished such amazing achievements. Lord Bacon, after listing in his precise and orderly manner all the various ways that we may be guided in our researches by theory, observation, and previous experiment, concludes quite unexpectedly by adding a new category, what he calls the experiments of a madman, and defines as follows:

> When you have a mind to, try something not because reason or some other experiment leads you to it, but simply because such a thing has never been attempted before. The leaving I say of no stone in nature unturned. For the magnalia of nature generally lie out of the common roads and beaten paths so that the very absurdity of the thing may sometimes prove of service. But if reason go along with it, that is, if it be evident that an experiment of this nature has never been tried, then it is one of the best ways and plainly shakes the folds out of nature.

The example Bacon gives of such unprecedented experiments is of peculiar interest to us:

> But of what I may call close distillation no man has yet made trial. Yet it seems probable that the force of heat, if it can perform its exploits of alteration within the enclosure of the body, where there is neither loss of the body nor yet means of escape, will succeed at last in handcuffing this Proteus of matter and driving it to many transformations; only the heat must be so regulated and varied that there be no fracture of the vessels.

> No one should be disheartened or confounded if the experiments which he tries do not answer his expectation. For though a successful experiment be more agreeable, yet an unsuccessful one is oftentimes no less instructive. And it must ever be kept in mind (as I am continually urging) that experiments of Light are even more to be sought after than experiments of Fruit.

What Bacon was "continually urging"—that "experiments of Light," those that lead to enlightenment on fundamental principles, "are even more to be sought after than experiments of Fruit," those that bring practical results—needs more than ever to be kept in mind at the present day, when public and employers are impatient of research that does not bring immediate and profitable returns. So it is worthy of notice that the example which Bacon cites as the experiment of a madman—that is, destructive distillation—has been peculiarly productive of both Light and Fruit. Applied to coal, it has given us coke for metallurgy, gas for cities and shops, and coal-tar products of innumerable variety and inestimable value. Applied to petroleum, it has increased the yield of gasoline by some 2,000,000 gallons a day. By thus "handcuffing this Proteus of matter and driving it to many transformations" we have gained an insight into the structure of the molecule and the chemistry of life.

An Agent for Democracy

Chemistry is the most effectual agent for democracy, since it actually accomplishes in regard to many material things that equality which legislation aims to bring about in the political sphere. Luxuries, formerly the monopoly of the privileged classes, become, through applied science, the common property of the masses. The "royal purple" of the ancients and dyes far more beautiful are now to be had on the bargain counter, and Solomon in all his glory was not arrayed like the modern American maiden. Even though her purse be scant she need not lack jewels and perfumes and fine raiment such as once were worth a slave's life. In early ages the man who owned a piece of steel shaped it into a sword and made himself master of his fellows. Now we make buildings out of steel and he who lives in the garret of one of them could look down on the tower of Babel. The Feudal Age vanished at the first whiff of gunpowder, for that device of the Black Art leveled the natural and the artificial inequalities of humanity in warfare, for with a gun in his hand the churl could meet the knight on equal footing and the dwarf was match for the giant—more than a match, for he had the larger target. Medicines such as a prince could not have procured, though his physicians surveyed the earth from China to Peru, are now at hand to cure the pauper. The new chemical motive powers have given man in the automobile a very fair substitute for the seven-league boots of the fairytale; they enable him to go down into the sea in ships on more or less lawful occasions, and they have endowed him with the wings that he has always longed for but never expected to get until he reached Heaven. Books are no longer chained up in treasuries but, manifolded by the magic of ink, are to be bought on the street corner like peanuts; pictures from the private gallery of prince or plutocrat are multiplied by the same mechanism and scattered throughout the land. We do not have to pay ten dollars to hear one song by Galli Curci since we can hear her at home with as many encores as we like. Caruso, though dead, yet speaketh. His voice has been embalmed by carbolic acid. Events that few could witness are brought to all of us on the celluloid film. So, whether it be the satisfaction of our material wants or the gratification of our aspiration for art and literature, the chemist acts as the agent of applied democracy. Democracy has been engaged in a struggle for life lasting five years and has emerged triumphant—thanks to the chemist. For war has now become essentially a branch of applied chemistry, carried on almost entirely by chemical weapons and chemical defenses. Germany, regarding herself as the heaven-born leader of mankind in this science, attempted to use it to establish her political supremacy in the world, but in spite of her advantage at the start she was foiled in the end by the democratic nations. She had freed herself in advance from dependence upon the nitrate beds of Chile for her explosives by developing methods of making nitrates from the air.

The war is over and Germany has been relieved by the Allies of the burden of armament that still weighs upon the victorious nations. But Germany, unlike the United States, finds it profitable to proceed with the Haber process even in time of peace. We need have no fear of such a catastrophe as the explosion of Oppau. If the Muscle Shoals plant should blow up now, the loss of life would be considerably less. It is curious to recall that the allied aviators were never able to blow up the Oppau works despite their gallant and persistent attempts, yet now the Germans without outside aid have removed the entire establishment from the earth with the greatest ease. The moral of this is the old maxim, "If a thing is to be done, do it yourself."

The Washington Conference on Reduction of Armament decided to prohibit the toxic forms of chemical warfare but not the explosive. Consequently, we cannot use gases against our foreign foes, though they may be still employed against our own people when disorderly. Even the comparatively mild lachrymatory and sternutatory gases are officially debarred. We may use chemicals to draw blood from our enemies but not to draw tears. Our military authorities seem determined that the American Army shall never be sneezed at.

Whether this paper prohibition will hold against an unscrupulous or desperate enemy or whether our soldiers may some day be caught unprepared as were the British at Ypres, must be left for time to determine. But since the chemists of the country are not responsible for the risk, they may rejoice in the meantime at being relieved of the distasteful task of devising modes of destruction and concentrate their attention upon the constructive side of their science.

SOCIOLOGICAL INFLUENCE

The chemist is not merely a manipulator of molecules; he is a manager of mankind. His discoveries and inventions, his economics and creations, often transform the conditions of ordinary life, alter the relations of national power, and shift the currents of thought, but these revolutions are effected so quietly that the chemist does not get recognition for what he accomplishes, and indeed does not usually realize the extent of his sociological influence.

For instance, a great change that has come over the world in recent years and has made conditions so unlike those existing in any previous period that historical precedents have no application to the present problems, is the rapid intercommunication of intelligence. Anything that anybody wants to say can be communicated to anybody who wants to hear it anywhere in all the wide world within a few minutes, or a few days, or at most a few months. In the agencies by which this is accomplished, rapid transit by ship, train or automobile, printing, photography, telegraph, and telephone, wired or wireless, chemistry plays an essential part, although it is so unpretentious a part that it rarely receives recognition. For instance, the expansion of literature and the spread of enlightenment which put an end to the Dark Ages is ascribed to the invention of movable type by Gutenberg, or somebody else, at the end of the 14th century. But the credit belongs rather to the unknown chemist who invented the process of making paper. The ancient Romans stamped their bricks and lead pipes with type, but printing had to wait more than a thousand years for a supply of paper. Movable type is not the essential feature of printing, for most of the printing done nowadays is *not* from movable type, but from solid lines or pages. We could if necessary do away with type and press altogether, and use some photographic method of composition and reproduction, but we could not do without paper. The invention of wood-pulp paper has done more for the expansion of literature than did the invention of rag paper six hundred years ago.

For the conveyance of ideas the picture is often more effective than the word and here the photographic processes of multiplication due to the chemist are the essential factors.

It is interesting to live at a time when we can witness the birth of a new art. Such was the last quarter of the fifteenth century when the art of printing books was being developed. Such is the first quarter of the twentieth century when the art of depicting motion is being developed. In fact, the moving picture has a better title to the term "a new art" than had printing, to which it was applied so long ago. Printing was not so much a new art as a mechanical extension of an old art, one of the oldest and best developed of the fine arts, the art of calligraphy. The first printed books were but cheap and inferior imitations of the handsome handwritten volumes of that day. Even to-day with four hundred and fifty years of progress it is in cheapness and convenience rather than beauty that the modern book surpasses the ancient manuscript

Now in the same way the moving picture does for the drama what printing did for literature, that is—it brings it within reach of the multitude through a process of mechanical manifolding. But it does something vastly more important than this. It makes possible for the first time the unlimited reproduction of actual events. This world of ours is a moving world and no static art can adequately represent it. There is no such thing as still life, or still anything else in the whole universe. Everywhere and always there is motion and only motion and any representation of reality at rest is a barefaced humbug. The more realistic the painting or sculpture the more obvious the failure. Myron's "Discobolus" and Meissonier's "Friedland" are as unnatural and fictitious as a centaur or a hippogriff. The most beautiful painting ever put on canvas, the finest statue ever carved, is a ridiculous caricature of real life compared with the flickering shadow of a tattered film in a backwoods nickelodeon. We have now for the first time the possibility of representing, however crudely, the essence of reality—that is, motion. Bergson has shown us what a paralyzing influence static conceptions of reality have had upon the history of philosophy and how futile have been all attempts to represent movement by rest. The scientist of to-day thinks in terms of motion. All modern thought is assuming kinetic forms and we are coming to see the absurdity of the old ideas of immutability and immobility. A similar revolution is impending in art. At least we glimpse the possibility of a new form of pictorial art, which, if capable of development as it seems to be, will make our present pictures appear as grotesque as the reliefs carved on Egyptian tombs or the scrawls on the caverns of Altamira. What will our posterity, familiar with moving portraiture, think of our admiration of Mona Lisa's smile, frozen on her lips for four centuries? A smile is essentially a fleeting thing, an evanescent expression. A fixed smile is not a smile at all but a grimace. It is only by the most violent effort of the imagination that we can ignore the inherent artificiality and limitations of painting sufficiently to get from it the illusion of reality.

METAPHYSICS OF CHEMISTRY

In considering the contributions that chemistry has made to our wealth and comfort, we must not forget that every fundamental discovery alters also our attitude toward life and consequently our conduct. There is a metaphysical as well as a physical side to chemistry. The new conceptions of the atom and of the sidereal universe, of matter and energy, of time and space, developed within the last ten years, will inevitably transform the prevailing modes of thought in philosophy, religion, and sociology as much as did the Copernican idea of the moving earth in the fifteenth century and the Darwinian idea of developing species in the sixteenth century.

The theory that the heat of the stars comes not from gravitational contraction but from such intra-atomic sources as the formation of helium from hydrogen has extended the life of our sun by some thousands of millions of years, and thereby the limitation of life on the earth and the possibility of the development of a superior civilization. So we don't have to hurry so hard as we did when we thought that the sun was a guttering candle, likely soon to flicker out and leave us in the dark and cold. We used to watch with anxiety the periodical reports of Langley and Abbot as to the constancy of the solar constant in order to see how much more time we had to perfect our social system before night, for when we looked at the daily papers we did not seem to be making progress very rapidly and it looked as though we should all be Eskimos before we got our society to suit us.

The mind is supposed to be immaterial but it seems to be possessed of inertia. The more quickly you want to move the mind of man the greater the power that it is necessary to apply. To move the mental mass of the nation greatly requires almost infinite expenditure of energy or almost infinite time. Since scientific men devote very little energy to the propagation of their views, it takes a very long time for new scientific ideas to act upon the popular mind. There is consequently a lag in the progress of civilization, a break in the line of march between the vanguard and the rank and file.

This is largely due to the lack of efficient terminal facilities in the delivery of intelligence. Transportation experts tell us that often a larger part of freight charges is consumed in the short haul between station and home than in the long haul by ship or train. So it is in the transmission of ideas. An idea may be sent around the world at the rate of 186,000 miles a second, but the short haul between the eye or ear and the brain may require twenty years. If the message is in a foreign language, such as scientific terminology, and there is no translator about, the reception of the intelligence by the average mind may be indefinitely delayed.

Need for Popularization

Chemistry has long since abandoned the pretension of being a secret science but it has not yet become a public science. It has the air of being much harder to understand than it really is. Its symbols are almost as repellent to unfamiliar eyes as are the mathematical signs of physics. The verbal formulas, by which compounds are designated, are mistaken for names and considered unpronounceable. But such impediments to popularity are not peculiar to chemistry. Other sciences, quite as much handicapped by strange nomenclature and recondite conceptions, are nevertheless read with eagerness by the public. Astronomy, which is largely mathematical and has no practical value for the reader and does not deal with human beings or any living thing, is still one of the most popular of the sciences. We have to put an astronomical article into our Science News Bulletin every week to satisfy the newspapers to which it is syndicated, but if we omit a chemical article we get no complaints.

One reason why the public is not so much interested in chemical research as it ought to be is the lack of writers willing to translate the science into ordinary English and present it in an attractive style. I speak with some assurance on this point for it has been my business, ever since Science Service was founded a year and a half ago, to hunt for people trained in the several sciences who can and will write about them for newspapers and magazines, and I have found it more difficult to get good writers in chemistry than any of the other sciences. Yet there are more chemists in the country than any other scientists. Not all of them are so absorbed in research, teaching, or industry, that they could not find a leisure hour for writing once in a while. I can find plenty of people to write about birds or bugs, clouds or stones, crinoids or endocrines, stars or starfish, but I find few who will tell the thrilling continued story of chemical discovery.

Yet no science touches human life more intimately than chemistry. None is of more practical importance in industry. None is turning out more sensational novelties. None has a more varied and romantic history.

Of its technical literature chemistry may well be proud. The three journals of this Society, and especially our system of abstracts, are the envy of all the other sciences, and there are various other able and attractive journals of chemical science and industry. But these are read exclusively by chemists and there is no popular periodical of chemistry published anywhere in the world. In the popular science periodicals and in the scientific articles of the general magazines, chemistry does not fill as large a space as its practical importance and intrinsic interest demands. At least so it seems to a chemist. The chemical news service of this Society is doing a splendid work in spreading chemical information through the newspapers, and the Local Sections are bringing our science to the attention of the public by their meetings, but there is need for other kinds of chemical literature, especially for magazines and books. Last year the Washington Academy of Sciences prepared, at the request of the Washington Public Library, a list of One Hundred Popular Books in Science. In many fields, such as botany, astronomy, paleontology, entomology, and the like, there was an embarrassment of books to choose from, but when it came to the science of chemistry Dr. Sosman, chairman of the committee, reported that not one could be found. There were several popular books on special topics, such as the chemistry of commerce, industry and everyman's life, but none that treated the science as a whole and satisfied the requirements of the selection, which were that the book should be readable by the ordinary reader, not a textbook, not a reference book, not a home study course, but so written that it would interest one who had no previous knowledge of the subject and no special reason for wanting to know about it. It is worthy of note that the committee had to go abroad for some forty per cent of its popular science books, and that several of them were over fifty years old, although a recent book would be preferred. Yet some of these British books find their greatest sale in the United States, notwithstanding the advantage that an American writer has in local references and colloquial language. It would seem that a hundred million readers might reasonably expect to have one popular book in each science once in fifty years in order to keep within sight of scientific progress.

I would not take up so much of your time with my business, but it is your business too—at least I hope to persuade you that it is. I am glad to see that you have already taken a step that will aid in the popularization of the science by organizing a Section of History of Chemistry. For one of the reasons why science is caviar to the general, is that it has been so conscientiously depersonalized. The effort is constantly made to reduce science to a set of mathematic formulas, free from all taint of time, place, and personality, bearing no trace of its erratic history and early gropings in the dark. This is quite a proper procedure for the development of the science, no doubt, but it has the unfortunate effect that in eliminating the human element you have eliminated the human interest. C. P. sucrose is a beautiful product, a triumph of technology in which the Division of Sugar Chemistry may well take pride, but it is not so tasty as maple sap or cane juice. It has lost its vitamins. That, I think, is why pure science is distasteful to the layman. It has lost its vitamins To put a modern high-grade textbook in the hands of the ordinary reader is like feeding decorticated rice to a soldier. It gives him mental beriberi. I hope I will not be misunderstood as saying anything against the chemist's constant efforts to achieve a higher degree of purification. Perfect purity is a noble aim even though it be asymptotically unattainable to human beings. There was once a little girl who prayed "O God, make me pure; make me absolutely pure like Royal Baking Powder!" Now it does not do any harm for baking powder to be pure because it gets mixed with so many other things, but if the flour is absolutely pure, and the fat and the salt and the water, well, somehow the bread is not so nutritious as it might be.

I am not sure that even in a textbook a bit of history or a few personalities would be out of place, though they might give the student the idea that the principles of the science have been worked out by slow degrees and much blundering by fallible human beings instead of being handed down in perfect form on tables of stone like the Ten Commandments. But anyhow, I am sure that for the general reader it is best not to refine too highly but to leave in a little of the human alloy. And I hope that your Section of History will develop some young writers who will turn out a readable character sketch of the creators of chemistry, or a dramatic description of how their discoveries were made and what they mean to the world. One can get such "human interest stories" in abundance about authors, artists, musicians, statesmen, and warriors, but I have been searching in vain for writers who would do as much for science. Until such writers are found we cannot expect readers in general to take as much interest in science as they do in literature, fine arts, politics, and war.

The Chemical Control of Gaseous Detonation with Particular Reference to the Internal-Combustion Engine

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AN EXTENSIVE study of gaseous detonation has been made by a number of investigators, but in spite of this fact the phenomenon is as yet not well understood. In presenting this paper, therefore, we will not attempt to explain all the phenomena with which it deals. The object of the paper is to discuss the bearing of this factor on the operation of internal-combustion engines, and to describe the progress that has been made in controlling it by chemical means.

FRUITS OF EARLY STUDY OF GASEOUS DETONATION

In 1881 Bertholet[2] and LeChatelier[3] independently discovered that the propagation of flame through mixtures of some combustible gases with air, and through mixtures of practically all combustible gases with oxygen in proper proportions, results in setting up a detonation wave. These results were confirmed by H. B. Dixon,[4] who has carried out quite an extensive investigation of this subject. Mallard and LeChatelier[5] noted that the development of the detonation wave is not progressive, but always instantaneous. They noted further that the detonation wave is characterized, not only by its great velocity of movement, but also by its intense luminosity. Dixon[6] was also impressed by the sharpness with which luminosity is set up when detonation occurs. Bertholet and Vieille[7] and also Dixon[4] showed that the velocity of the detonation wave is constant, and Dixon advanced the theory that during detonation the flame travels at the same speed as sound at the temperature of the burning gases. Mallard and LeChatelier[7] found that very large pressures are developed by detonation waves, but that such pressures exist only for an exceedingly brief period. This finding was confirmed by Dixon,[4] who worked on the principle that, if a pressure is produced in a glass container greater than the glass will withstand, the vessel will be broken, although the pressure may endure only for a very short interval of time. Dixon gave a range of from 25 to 78 atmospheres for the magnitude of these pressures for various gases. He showed further that these instantaneous pressures are approximately four times the maximum "effective pressure" developed by the explosion.

GASEOUS DETONATION AN IMPORTANT FACTOR IN INTERNAL COMBUSTION

Except for some comparatively recent work, practically all the study of gaseous detonation that has been made has been conducted in atmospheric tubes, or under other conditions that did not simulate those of internal combustion. From an economic standpoint, however, the detonation that occurs in internal-combustion engines is of great importance.[8] Nearly everyone who has driven an automobile is familiar with the troublesome "pinking" in the engine which is known as a "knock." The knock is a sharp ringing noise, suggestive of two metallic parts striking together, and is most pronounced when the engine is pulling at slow speeds in high gear, as is the case on steep grades or when accelerating from slow speeds. This noise is not caused by the striking of metallic parts, but it has been fairly well established that it results from a detonation of the highly compressed fuel mixture in the combustion chamber.

For any given fuel the intensity of detonation varies with the compression of the engine—the higher its compression the more pronounced the detonation. It is herein that the seriousness of detonation in internal-combustion engines lies, for both the torque and the fuel economy of an engine are increased as its expansion ratio (called in automotive practice "compression ratio") is raised. While the detonation that occurs in automobile engines of present compressions is so slight as to be merely an unpleasantness that does little or no harm, in engines of highly economical compressions its intensity becomes so great as to result not only in loss of power but also in actual damage to the engine. This phenomenon of detonation, then, stands as an effective barrier to the obtaining of better fuel economies from internal-combustion engines, and because of this fact, it has an important economic aspect.[9]

Detonation as it occurs in internal combustion does not vary with the compression of the charge alone. It varies directly with the temperature, and is aggravated by advance of the spark timing and by carbon deposits in the engine. It is further influenced by certain elements of design, such as the shape of the combustion chamber and the location of the spark plug, but of great importance is the fact that it is a function of the chemical structure of the fuel. As an illustration of this the case isomeric compounds ether and normal butyl alcohol may be cited. These compounds may have the same ultimate composition, $C_4H_{10}O$, but they differ widely in molecular structure. Ether detonates when burned at a very low compression; alcohol, when burned at a compression and temperature which are relatively very high, is entirely free from detonation. Similarly, ethylenic hydrocarbons have a greater tendency to detonate than saturated cyclic hydrocarbons of the same ultimate composition.

While these facts are interesting and important, the situation with respect to automotive fuels in the United States is that their composition is fixed within fairly narrow limits. From the standpoint of available supply, petroleum oils must be used as the principal source of motor fuels for many years to come. From a commercial standpoint, therefore, the problem is to find a means of controlling the detonation of paraffin hydrocarbons, a tendency which becomes more pronounced as their molecular size increases, or their volatility decreases.

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[1] [illegible] General Motors Re[illegible]

[2] [illegible] 93 (1881), 18.

[3] [illegible] 93 [illegible]

[4] [illegible]

[5] [illegible]

[6] [illegible]

[7] [illegible]

[8] [illegible] detonation from the [illegible] may be found [illegible] 9 (1911), [illegible] p. 221. Woodbury, [illegible] 8 (1921), 599. H. R. Ricardo, *Automobile Engineer (England)*, 11 (1921), 51, 92, 130, 169; *J. Soc. Automotive Eng.*, **10** (1922), 305. Thomas Midgley, Jr., *Trans. Soc. Automotive Eng.*, [2] **15** (1920), 659; *J. Soc. Automotive Eng.*, **10** (1922), 357. T. Midgley, Jr., and T. A. Boyd, *Ibid.*, **10** (1922), 7, 451; THIS JOURNAL, **14** (1922), 589.

[9] For a more complete discussion of this phase of the subject see "The Application of Chemistry to the Conservation of Motor Fuels," Midgley and Boyd, THIS JOURNAL, **14** (1922), 849.

THEORIES OF DETONATION IN INTERNAL COMBUSTION

In spite of the fact that gaseous detonation is not well understood, many theories have been advanced to explain the phenomena that occur in internal-combustion engines variously known as "detonation," "knock," and "pinking." Aside from those which may be classified as mere speculations, three theories have been advanced in definite form.[10]

The first of these, known as the mechanical knock theory, explains the sound as resulting from an actual impact between parts of the engine, such as between cylinder wall and piston or between shaft and bearings. This theory does not attempt to explain the cause of pressures which must exist in the engine cylinders to produce these mechanical impacts. For this reason it may be passed over with this simple mention.

A second theory is that which explains the sound and attendant phenomena of detonation as resulting from a very rapid increase of pressure in the engine cylinder.[11] According to this theory, a portion of the charge is compressed to its auto-ignition point by the expansion of the portion first ignited, which compresses before it the unburned part of the charge. When the rate of increase in temperature due to this compression exceeds by some margin the rate at which a sufficient amount of the heat can be dissipated to the cylinder walls, the remaining portion ignites spontaneously and nearly simultaneously throughout. This theory apparently implies that a fuel should have a tendency to knock that is proportional to its spontaneous-ignition temperature.

The third theory explains the phenomena incident to the fuel knock as resulting from the impact of a high-velocity, high-pressure wave against the cylinder walls and head. It has previously been demonstrated mathematically that, during the passage of a flame through a combustible mixture in a closed container, a higher pressure must exist immediately in front of the flame front than behind it, and that this pressure difference may be represented by the following expression:[12]

$$P_1 - P_2 = \frac{W^2}{g}(V_2 - V_1) \qquad (1)$$

where P_1 is the pressure in front of the flame
P_2 is the pressure to the rear of the flame
W is the reaction velocity expressed in pounds of mixture entering the flame front per second
g is 32.2
V_1 is the specific volume of the mixture in front of the flame
V_2 is cu. ft. per lb. of burned mixture to the rear of the flame front

Physical chemistry tells us that

$$W \text{ should equal } C D^n T^m \qquad (2)$$

where C is a constant
D, density of the mixture
T, absolute temperature
n, exponent the numerical value of which depends upon the chemical equations of combustion
m, exponent the numerical value of which must be determined experimentally

By combining Equations 1 and 2 and substituting thermodynamic equivalents, the following equation is obtained:

$$P_1 - P_2 = \frac{AP_1^q}{P_1 - P_2} + BP_1^n - CP_2 \qquad (3)$$

where $A = 2JHL$
$J = 778$
H = effective heat value per pound of mixture
$L = \frac{W_o^2}{P_o^q \times g}$
$W_o = KD_o^n T_o^m$ $\quad q = \frac{2[n + m(\gamma - 1)]}{\gamma}$
$g = 32.2$
$B = \frac{2K^{\frac{1}{\gamma}} L}{\gamma - 1}$
K = constant of adiabatic compression
$= P_1V_1^\gamma$
$N = q - \frac{1}{\gamma}$
$C = \frac{2\gamma}{\gamma - 1}$
γ = ratio of the specific heats

This Equation 3 should represent the relation between the pressure in front of the flame and that to its rear at all times. It is, therefore, an expression for the pressure in the wave of detonation ($P_1 - P_2$). Values for n and m must be determined experimentally for each different fuel. But, if values be ascribed to n and m, and the relation of P_1 to P_2 be plotted, it will be observed that below some critical value for P_2 the pressure difference is merely nominal, but that at this critical value P_1 is rising at an infinite rate. Above the critical value for P_2 the equation is only satisfied by P_1 = infinity, which in a physical sense means a large difference of magnitude such as 50 to 100 times P_2.

The above Equation 3 affords a basis for the explanation of the phenomena incident to detonation. During normal combustion the pressure differential is almost insignificant, its magnitude being less than one pound per square inch, but in the case of a flame front moving at the velocity of sound with respect to the burning gases, the pressure differential becomes enormous. If P_1 = infinity, P_2 may be any value large or small, so that during detonating combustion the flame front is preceded by a region of dense gas at an extremely high pressure. According to this theory, the metallic sound, commonly called the knock, is caused by this high-pressure, high-velocity wave striking the top or sides of the combustion chamber.

If the second or auto-ignition theory gives a correct explanation of detonation, the only means of controlling detonation under a given set of conditions would be to raise the spontaneous-ignition temperature of the fuel. If the third or high-velocity, high-pressure wave theory is correct, detonation may be controlled by affecting the reaction velocity of combustion. The history of contact catalysis indicates that there should be negative combustion catalysts, very small percentages of which would exert a large effect on the reaction velocity of combustion. Although such a method of reasoning might well have served as the basis of search for a material to negatively catalyze combustion, the actual discovery of materials that exert just such an effect preceded the development of the high-velocity, high-pressure wave theory, it having been an outgrowth of many attempts to explain the remarkable behavior of these substances. In view of the very small amounts of some compounds that need be present in a combustible mixture in order to prevent detonation, as is shown below, it does not seem possible to account for their behavior on the basis of the auto-ignition theory of the knock. However, on the basis of a negative catalytic effect on the reaction velocity of combustion, the behavior of the materials discussed in this paper is in agreement with the high-velocity, high-pressure wave theory of detonation.

CONTROLLING DETONATION BY CHEMICAL MEANS

It has been found that detonation can be either suppressed or induced by the presence of very small amounts of certain materials in the combustible mixture. These substances may be dissolved or suspended in the fuel, or they may be admitted to the combustion chamber in some other way. The action of practically every type of compound that should affect detonation has been tried, and a large number have been found to possess the property of affecting combustion in such a way as either to suppress or induce detonation.

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[10] Dickinson, *J. Soc. Automotive Eng.*, **8** (1921), 558.

[11] H. R. Ricardo, *The Automobile Engineer (England)*, **11** (1921), 92; *J. Soc. Automotive Eng.*, **10** (1922), 308.

[12] T. Midgley, Jr., *J. Soc. Automotive Eng.*, **10** (1922), 361.

TABLE I

ELEMENT	TYPICAL COMPOUND	EFFECT ON REACTION VELOCITY OF COMBUSTION
Iodine	Elemental	Retards
Bromine	Elemental	Accelerates
Chlorine	Elemental	Accelerates
Nitrogen	$C_6H_5NO_2$ or $C_2H_5NO_2$	Accelerates
Nitrogen	$C_6H_5NH_2$	Retards
Selenium	$(C_2H_5)_2Se$	Retards
Tellurium	$(C_2H_5)_2Te$	Retards
Tin	$(C_2H_5)_4Sn$	Retards
Lead	$(C_2H_5)_4Pb$	Retards

If the high-velocity, high-pressure wave theory of detonation is correct, the action of these materials is to affect the reaction velocity of combustion in such a way as either to accelerate or retard the tendency of the combustion to reach the velocity of detonation. Because of this effect, substances which, when present in small percentages, exert a powerful suppressing action on detonation have been termed "antiknock materials" or "compressionizers." Thus, diethyl telluride is an antiknock material, but benzene is not. Although benzene, if present in sufficient concentration, removes the tendency of kerosene to detonate at compressions which are used commercially, it apparently does so simply by virtue of the fact that it itself is a fuel that will withstand a very high compression without detonating. Benzene does not detonate even when burned at compressions of more than 200 lbs. per sq. in., so that, when it is blended with a kerosene, the resulting mixture partakes of the nondetonating property of benzene to the extent to which benzene is present in the mixture. This is evidently not the case with diethyl telluride, however, of which 0.1 per cent by volume is equivalent in its effect on detonation to about 25 per cent by volume of benzene. Diethyl telluride exerts this remarkable influence on the combustion of a kerosene-air mixture, although in this case it is present in only the very small ratio of 1 molecule to about 50,000 molecules of total mixture.

It is not within the scope of this paper to present detailed data on all the antiknock materials that have been studied, especially since the investigation has not been completed, but the results that have been obtained may be summerized in general terms. The compounds which have been shown to possess this property of affecting the reaction velocity of combustion to a marked degree are chiefly derivatives of about fifteen elements, but we have found that antiknock substances are not limited entirely to compounds of these fifteen elements. Oxygen and the halogens in the elemental form exert a marked effect on combustion, iodine being an antiknock material, and the other elements inducing detonation to different degrees. A considerable number of the common compounds of these elements exhibit similar properties. A great many nitrogen compounds are effective antiknock materials, probably the best of which are the aromatic amines. Certain compounds of selenium, tellurium, tin, and lead, are remarkably effective for the suppression of detonation. Some compounds of arsenic, antimony, and phosphorus have a marked but lesser effect for preventing detonation. Table I shows the nature of the effects of some of the more important of these substances on the reaction velocity of combustion.

A compilation of the relative effects of a number of antiknock materials is given in Table II. Benzene is used as a basis of comparison, and relative values are given for the various materials on the volume and the molecular bases. From the table it may be seen that, when compared with benzene in 25 per cent concentration in kerosene, 1 volume of diethyl telluride is equivalent in effect to 250 volumes of benzene, and 1 volume of lead tetraethyl is equivalent to about 625 volumes of benzene. If comparison be made on the molecular basis, the figures show that 1 molecule of diethyl telluride is equal in effect to 330 molecules of benzene, and that 1 molecule of lead tetraethyl is equivalent in effect to over 1400 molecules of benzene. A better impression of how small an amount of some of these materials need be present in a combustible mixture in order to exert a marked influence on the character of the combustion may be gathered from the values given in the last column of Table II. Thus, for a theoretical mixture of kerosene and air, assuming that the average molecule of the kerosene is $C_{13}H_{28}$, 1 molecule of lead tetraethyl in 215,000 molecules of total mixture exerts an influence on the tendency of the fuel to detonate which is equivalent to about 25 per cent of benzene in the kerosene. In view of the exceedingly small amount of this material that is present in the reaction mixture, it exerts an influence on the character of internal combustion, which is so powerful that it at least bears a close analogy to a catalyst.

TABLE II—A COMPILATION OF THE RELATIVE EFFECTS OF A NUMBER OF COMPOUNDS FOR SUPPRESSING DETONATION AS COMPARED WITH BENZENE

ELEMENT	COMPOUND	Per cent by Volume in Kerosene Required to Effect a Given Suppression of Detonation	Number of Gram Molecules in Resulting 355-Cc. Mixture with Kerosene to Give Equal Suppression of Detonation	Approx. Number of Mols of Theoretical Fuel-Air Mixture in Which 1 Mol Exerts an Effect on Detonation of a Given Magnitude[1]
	Benzene	25.0	1.0[2]	150
Iodine	C_2H_5I	1.6	0.07	2,150
Nitrogen	Xylidine	2.0	0.059	2,600
Tin	$(C_2H_5)_4Sn$	1.2	0.021	7,100
Selenium	$(C_2H_5)_2Se$	0.4	0.013	11,750
Tellurium	$(C_2H_5)_2Te$	0.1	0.003	50,000
Lead	$(C_2H_5)_4Pb$	0.04	0.0007	215,000

[1] The computations of these values have been made on the basis of a kerosene having $C_{13}H_{28}$ as its average molecule.

[2] 25 per cent by volume.

ILLUSTRATIONS OF EFFECTS OF ANTIKNOCK MATERIALS ON DETONATING COMBUSTION

The effect of the presence of a small percentage of diethyl selenide on the combustion of a detonating mixture of acetylene and air is very marked. An apparatus suitable for demonstrating this effect is shown diagrammatically in Fig. 1. The diameters of the gas holders bear such a relation to each other that a mixture of acetylene and air of proper degree of richness for maximum detonation[13] is forced into the explosion tube shown at the bottom of the sketch by water flowing from the upper container and displacing the gases from their respective holders. The mixture is formed in the end of the explosion tube where the outlet tubes from the gas holders enter the same chamber. The mixture passes through this metal chamber which is provided with a spark plug, and thence into the glass explosion tube. The closing of the valve in the chamber at the end of the explosion tube automatically completes the ignition circuit, and thereby ignites the mixture in the explosion tube.

As a means of introducing diethyl selenide to the acetylene-air mixture when desired, the valve in the gas line through the wash bottle is opened. An orifice in the by-pass tube permits a small amount of the air to pass through the wash bottle which contains the vapor of diethyl selenide. At 22° the vapor pressure of diethyl selenide is about one-twentieth of an atmosphere.

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[13] Detonation is said to be most easily initiated in an acetylene-oxygen-nitrogen mixture that contains only sufficient oxygen to give carbon monoxide. Woodbury, Lewis and Canby, *J. Soc. Automotive Eng.*, **8** (1921), 215; H. B. Dixon, *Ibid.*, **9** (1921), 237.

The size of the orifice is such that, when the valve in the by-pass is open, diethyl selenide constitutes about one-seven-hundredth of the volume of the mixture entering the explosion tube. This amount is so small that it cannot affect the combustion by combining with either of the reacting materials, or by entering into the reaction in the ordinary sense.

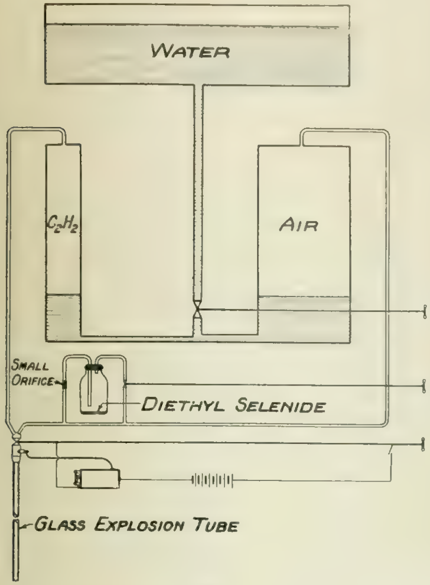

FIG. 1

APPARATUS SHOWING THE EFFECT OF THE PRESENCE OF AN ANTIKNOCK MATERIAL ON THE COMBUSTION OF ACETYLENE IN A TUBE AT ATMOSPHERIC PRESSURE

The demonstration shows that with acetylene and air alone detonation is set up after the flame has traveled only a short distance along the tube, as is evidenced by the luminosity, and by the sharp "crack" that is produced by the pressure wave resulting from the detonation. But when diethyl selenide is admitted with the acetylene-air mixture, the burn is quiet and it lacks the high degree of luminosity that characterizes detonating combustion.

The effect of the presence of an antiknock material on combustion is even more striking under the actual conditions of internal combustion. A single cylinder engine having a high compression ratio, preferably around 5.3 : 1, is suitable for use in this test.[14] The engine should also be fitted with an apparatus for indicating when the combustion is a detonating one. Such a device, called the bouncing-pin apparatus, has been described and shown diagrammatically in previous publications.[15] The bouncing-pin element consists of a steel pin resting by gravity on a piston. The bottom of this piston comes flush with the inner surface of the cylinder head, and its vertical movement is resisted by a heavy spring. Immediately above the upper end of the pin, contact points are held in position in an electric circuit in such a way as to be closed when the pin is thrown free of the piston. During normal combustion, when there is no detonation, the pin moves up and down with the piston, the amplitude of movement of which is only a few thousandths of an inch. But when detonation occurs, the disturbance in the combustion chamber is of such a nature that the pin is thrown free of the piston, closing the contact points. This completes the electric circuit, and during the period that the contact points are closed, current flows through the lamp and the electrolytic cell. If the detonation is continuously repeated and of sufficient violence, the lamp filament becomes luminous, but even a slight or discontinuous detonation causes the evolution of gas in the electrolytic cell. The quantity of gas generated in a given number of revolutions is a measure of the intensity of detonation.

When this engine is run on commercial gasoline alone, a violent detonation occurs, which imparts considerable luminosity to the filament of the lamp. The detonation also manifests itself by the loud and sharp metallic sound in the engine, and by the large volume of gas generated in the electrolytic cell. If, while running under this condition, a small amount of the vapor of diethyl selenide (simply that arising from a bottle containing liquid diethyl selenide) be admitted with the air entering the combustion chamber, the detonation is entirely eliminated, and the power output of the engine rises to normal, or to the extent that it had been cut down by the detonation.

If the same engine be run on a mixture of about 35 per cent benzene in commercial gasoline, very little, if any, detonation will be noted. A violent detonation is induced, however, when an unstoppered bottle containing a volatile nitrate or nitrite, such as isopropyl nitrite, is held close to the air inlet of the engine. The intensity of this detonation may easily be made so great as to result in stopping the engine altogether. Bromine may be substituted for the nitrite in this test, but it is only about one-half as effective for inducing detonation.

These materials are equally effective when admitted with the fuel, either in solution in the fuel or by injection along with it. In this engine, having a compression ratio of 5.3 : 1, which gives a compression around 115 lbs. per sq. in., the detonation when running on commercial gasoline alone is so violent that it results in a large loss in the power of the engine. But when a very small amount of tetraethyl lead, around 0.1 per cent by volume, is present in the gasoline, the engine runs with such perfect smoothness that no gas is generated in the electrolytic cell, and the power of the engine comes back to normal. Computation shows that this result is accomplished simply on account of the presence of 1 molecule of lead tetraethyl in over 80,000 molecules of total mixture.

A CONCEPTION OF THE ACTION OF ANTIKNOCK MATERIALS

The action of antiknock materials, such as diethyl selenide or lead tetraethyl, appears to be that of preventing combustion from becoming abnormal by accelerating to the velocity of detonation. It is inconceivable that this effect can be due to an energy factor; because, as has been shown (Table II), the presence of as little as 1 molecule of one of these materials in over 200,000 molecules of a combustible mixture of kerosene and air exerts an effect in the suppression of detonation equivalent to 25 per cent of benzene by volume in kerosene.

These materials appear to have an effect on the chemical reaction, combustion, that is closely parallel to that of the class of substances called catalytic agents. Thus, very small amounts of these substances are required to exert a remarkable influence on combustion. Also, in the case of the most powerful antiknock materials, the effect does not increase indefinitely in proportion to the amount present, but, as concentrations which are relatively high are reached, the curve of effect tends toward an asymptote to a maximum. A further analogy between catalytic agents and these substances lies in the fact that the antiknock material apparently does not affect the final state of equilibrium, except in so far as by retarding the reaction velocity of combustion it tends to insure its completeness. The analogy breaks down to some extent on the criterion that the chemical composition of the catalytic agent is unchanged at the completion of the reaction process. However, antiknock materials are for the most part combustible, and the conditions to which they are subjected are extremely severe. On the whole, it appears that the action of these substances, which have been termed Antiknock Materials or Compressionizers, bears considerable analogy to that of catalytic agents.

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[14] The compression ratio of an engine is the ratio of the volume above the piston when it is in its extreme lower position to the volume above the piston when it is in its extreme upper position. The compression ratio of automobile engines at present is about 4.25 : 1. In this connection attention is again called to the fact that the intensity of detonation increases with the compression ratio of the engine.

[15] Midgley and Boyd, *J. Soc. Automotive Eng.*, **10** (1922), 7, and THIS JOURNAL, **14** (1922), 589.

Iridescent Colors in Feathers[1]

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At the Rochester meeting I reported on the structural blues in feathers. That left the metallic or iridescent colors to be accounted for. Michelson[2] believes that the colors in the tail of the peacock and the throat of the humming bird are due to selective reflection, like the yellowish green metallic color of solid magenta. Lord Rayleigh[3] maintains that the colors are the interference colors of thin films, often referred to as Newton's rings. Since the question seemed to involve coöperative research by men representing different fields, the Heckscher Research Council made a grant to a committee consisting of Messrs. Bancroft, Chamot, and Merritt, representing physical chemistry, chemical microscopy, and physics. As an unofficial member representing ornithology, the committee has had the enthusiastic coöperation of Mr. Louis Agassiz Fuertes, who was really responsible initially for the starting of the whole investigation. The work of the committee has been facilitated by the courtesy of Prof. A. A. Allen of Cornell University and of Dr. Frank M. Chapman of the Natural History Museum, who have supplied us with many typical feathers. For the experimental work the committee has been fortunate in securing the assistance of Mr. Clyde W. Mason, assistant in chemical microscopy at Cornell University. It is to his skill and perseverance that the successful outcome of the investigation is due.

While the nonmetallic blues are always in the barbs, the iridescent colors are wholly in the barbules, the barbs in such feathers being a dark dull brown and showing no color effects. The iridescent colors are visible by reflected light from both surfaces of the features but cannot be seen by transmitted light. By transmitted light the feathers of the blue jay, the tail feathers of the peacock and the throat feathers of the humming bird show no more signs of brilliant colors than do the feathers of a crow.

There is not only no bright color to be seen by transmitted light in any metallic or iridescent feather, but no bright-colored pigment can be extracted by boiling with any organic liquid. If the dark or melanin pigment is extracted, the metallic color remains with little change until the dark pigment is practically all gone and can be detected even then when the feather is examined under the microscope. The change in color with changing angle of incidence is that corresponding to interference colors, and is much greater than with substances like magenta, showing selective reflection. In fact, the change of color with changing angle of incidence is practically negligible with magenta and the other pigments of this type. The natural conclusion is, therefore, that the iridescent colors are not due to selective reflection.

The colors of iridescent feathers belong to Newton's series of interference colors, being caused by a laminated or plate-like structure of the barbules, where the color originates. These barbules present broad, flat surfaces forming an approximately plane surface which exhibits the colors with great brilliancy. The cross section of the barbule shows a central pith or core about two microns thick, which appears to be of somewhat fibrous or granular character. Enveloping this core are three thin layers or laminae, of equal and uniform thickness, and seemingly in contact. The color originates in these three layers, each about 0.4μ thick, which make the barbule act as a multiple thin film. The laminated outer layer of the barbules is particularly characteristic, and was not found on the nonmetallic feathers of the same bird where these were available for examination. In all cases a definite structure is associated with metallic luster. The barbules are always broad and flattened, distinctly segmented, with blunt ends, and generally contain much more dark pigment than adjacent noniridescent barbules of the same feather. Altum[4] says that "the metallic luster is always associated with the peculiar, hard, and smooth texture. A blind man could easily pick out all the birds with metallic luster in a collection of any size." The relation between structure and metallic luster is so close that Mr. Mason was able to pick out from the collection of drawings of barbules in Chandler's paper[5] those which were of the metallic type. Comparison with the description of the coloring of the feather showed very few errors, even though the drawings cover almost all species and include many feathers not possessing any noniridescent barbules for comparison.

The thickness of these films is about the value calculated for the interference colors of the order observed in feathers, though the whole structure is too small for very accurate measurements. In all the iridescent feathers examined, the colors appear to lie in the upper second or third orders of the series, which include the most brilliant of the interference colors—yellow, and red in the upper second order, and dull purple, blue, green, yellow, and red in the third order. Since we have no good method of determining exactly the order of interference and isolated color reflected from a thin film, this is based on matching the colors of feathers with those of artificial films, the colors of which are of known order.

With increasing angle of incidence the color usually changes through two or three of the colors of the above series. The change is frequently from the blue to the red end of the spectrum, but this is not necessarily the case. The pigeon, for instance, has feathers which change from bluish green through red to yellowish green with increasing angle of incidence. Thickening of the color-producing films by swelling results in a color change toward a color listed in a series after the original color, for the order of the color is higher the thicker the film. Thinning by pressure or in fault bars results in a color of lower order (earlier in the series) than the original color of the barbules.

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[1] [illegible] Research, [illegible]

[2] [illegible] 21 [illegible]

[3] [illegible] 37 (191[illegible]

[4] [illegible] Ornithologie, 2 (1854), 19.

[5] [illegible]niversity of California Publications, Zoology, 13, No. 11 (1914–16).

Bleaching does not destroy the colors, because there is no bright pigment to be destroyed, but only a structure; and the iridescence is uninjured unless the structure is destroyed. The metallic luster and brilliancy of iridescent feathers is due to the dark brown pigment in them, which serves as a dark background for the interference colors. The exact distribution of this dark pigment is not certain; but apparently no special distribution is necessary to give the metallic luster, provided the essential structure is present, for the white, faintly iridescent, pigeon feathers become brilliant and metallic when dyed with a brown dye, though a detailed study of sections of the dyed barbules shows a rather uniform distribution of the dye instead of segregation in one underlying layer. It is possible that a neutral-colored, transparent, thin film may serve to some extent as its own dark background, producing brilliant colors and a metallic luster, as does a colorless film on a dark background. As a matter of fact, we get brilliant colors with thin films of asphaltum varnish.

The metallic colors can be duplicated very satisfactorily by putting a thin film of a colorless varnish over a dark pigeon's feather, but the result is more garish than the real feather, because the film spreads over the feather as a whole instead of over each individual barbule. The curvature of the barbules, with the resultant complexity of the surface of the feather, results in a softening and blending of the garish colors noticed in plane, thin films, because of the different angles at which different parts of the curved surface are viewed. This causes a mingling of the colors seen at normal and at other angles of incidence, giving added softness and richness of color. The slight local variations in the thickness of the color-producing film also contribute to this effect by causing a mottling of colors, which mingle and appear to the eye as the mean color of all the various hues. The color which we observe on the feather is thus the result of the mingling of a number of colors adjacent in Newton's series, which produce the effect of a single, softer color. No one can deny that the colors of thin oil films on a pavement are garish.

Variation in the thickness of the color-producing films explains the different colors often observed on a single feather, either in the form of a pattern, as in the case of the peacock, or in gradations of color, such as are seen in the feathers of the starling, purple grackle, *Lamprocolius phoenicopterus bispecularis*, and other birds. Such iridescent feathers show bands of colors which remind one very much of the colors produced by oil on an asphalt pavement. For instance, some of the feathers of the starling are iridescent reddish purple at the base shading to yellowish bronze at the tip; others are yellowish green at the base to greenish blue at the tip; while some feathers of the purple grackle shade from reddish purple at the base to blue, greenish blue, green, yellow-green, to yellow-bronze at the tips. These sequences of shades are undoubtedly produced by a gradual variation in thickness of the color-producing films, for the colors adjacent on the feather are always adjacent in Newton's series, and, moreover, the colors shift with increasing incidence, just as do Newton's rings, the shift or change in position of a given color being toward the thicker part of the film.

The grosser structure of the feather may influence the appearance of the iridescent colors very markedly. Not only the perfection of the surface formed by the overlapping of the distal barbules, but also the visibility of the color, are dependent on this. For example, the blue-green iridescent barbules of the peacock feather are present in the black center of the "eye;" but are arranged so that they are seen edgewise and their color ordinarily does not appear. The iridescent colors of many birds, particularly humming birds, are often visible only from a position in front of the bird, and are quite invisible when the head of the bird is pointed away from the observer. This, again, is due to the barbules which are so arranged that, instead of having their planes in the general plane of the feather, they are skewed or tilted somewhat, and lie normal to a direction toward the head of the bird, rather than in the plane of the feather. Consequently, they are seen edgewise from other positions, and give little or no color.

One marvels at the way in which these colors are produced with such uniformity on different feathers and different birds through successive generations, in spite of the fact that a very slight variation in the thickness of the films would alter the color effect greatly. The production of iridescence seems to present a most remarkable case of the regulation of an essential structure within very sharply defined limits, not only in numerous individuals but also through many successive generations. Perhaps more remarkable still is the case of the white peacock. We had hoped that the tail feathers of the white peacock differed from those of the ordinary peacock only in not having the dark pigment present, in which case dyeing the feather or painting the back of it black would bring out the brilliant metallic colors. This does not happen because the tail feathers of the white peacock do not have at all the same structure as those of the ordinary peacock. In spite of the absence of color and the complete difference in structure, the general pattern of the peacock feather has been preserved in the white peacock even though the effect is produced in an entirely different way. This must have some great biogenetic significance, though fortunately that is not a problem for the chemist.

When this work was begun, the committee believed strongly in Michelson's theory of selective reflection; but it was soon found that this theory could not be applied satisfactorily to the phenomena observed, and the conclusion was reached finally that Michelson was wrong and Lord Rayleigh was right. The iridescent colors of feathers are caused by thin laminae or films in the barbules which produce interference colors. No colors due to selective reflection have been detected in any of the metallic feathers which have been studied. The birds examined include:

Black Minorcas and Rhode Island Reds (*Gallus*)
Bronze-winged Pigeon (*Columbia phaps*)
Common Pigeon
Green Heron (*Ardea virescens*)
Wood Duck (*Aix sponsa*)
Mallard (*Anas boschas*)
Sommering Pheasant (*Phasanius sommeringi*)
Monaul Pheasant (*Lophophorus impeyanus*)
Golden Pheasant (*Thumalea picta*)
Chinese Pheasant (*Phasanius torquatus*)
Peacock Pheasant (*Polyplectrum bicalcaratum*)
Bronze-headed Trogon
Peacock (*Pavo cristatus*)
Mu[illegible] mexicana
Ptilopus puella
Ptilopus pulchellus
Lamprocolius phoenicopterus bispecularis
Purple Grackle (*Quiscalus purpureus*)
Jacamar (*Jacamerops aurea*)
Ruby-throated Humming Bird (*Trochilus colubris*)
Red Kingbird of Paradise
Wild Turkey (*Meleagris americana*)
Nettion brasiliense
Starling (*Sturnus vulgaris*)
Muscovy Duck (*Cairina moschata*)

Chemists in New Jersey have formed a Chemists' Frelinghuysen Club to support Senator Frelinghuysen in his candidacy for reëlection. The basis of the appeal is to be his sympathy for and service to the chemical industry.

The Journal Literature of Chemistry

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HUMAN progress is made by coöperation. This is a scientific and industrial age. The great factor for progress in science and industry is research. Coöperation in research is effected chiefly by means of the journal literature. Among scientists, and increasingly among men of industry, there is a notably fine spirit of coöperation and service which prompts the publication for the benefit of all of the results and conclusions from their experiments and experiences. In the production of this literature, in its distribution, and in its use, efficiency is obviously of great importance. There is much room for betterment. The amount of wasteful repetition of thought and effort (some duplication of work to be sure is desirable and profitable) that can be attributed to the slightness of our command of the accumulated knowledge of mankind is exceedingly large. The great need and value of coördinated, available information were discussed with a broad point of view by Dr. Charles L. Reese in his admirable address[1] before the American Chemical Society at Birmingham and the efforts and plans of the National Research Council in its Information Service towards the fulfilment of this need were described. These efforts deserve full support. Dr. Reese dealt with information as a whole and spoke mostly of needs. It is my purpose here to set forth a few more or less random observations from constant work with the journal literature of chemistry, which it is hoped may be helpful to individuals in their efforts to increase their personal efficiency in the use of this literature in its present condition and with available facilities. Skill in this direction is of great value to any chemist. Are not too many lacking in such skill?

To trace in detail the development of the journal literature of chemistry from the period when personal contact and correspondence were the only means of coöperation through the various stages up to the present time, or to attempt to classify this literature, as might be done in several ways, is beyond the limits of this paper. Suffice it to say that since 1665, when the first scientific journal, the *Philosophical Transactions of the Royal Society*, put in its appearance, there has been an accelerated increase in the number of journals of interest to the chemist, and the bulk of the accumulated material has become almost staggering in its proportions. At the present time there are over a thousand journals appearing which have at least some chemical interest. The vastness of the chemical journal literature, its rapid and continuous advance upon the frontiers of our knowledge, and its essentially unorganized state, are further arguments why the chemist should see to it that he learns how best to make use of the means which have been provided to make this sea of information navigable. Otherwise he is likely to be lost at sea.

Exactness in Writing

Many chemists are producers as well as users of chemical literature. While it is my purpose to speak chiefly of the use of the literature, may I call attention to one characteristic of chemical papers which our experience in the office of *Chemical Abstracts* leads us to believe ought to be bettered by chemists who write papers? That exactness in scientific work is of paramount importance is not likely to be questioned. The same careful precautions to insure exactness which are taken in their work in the laboratory are apparently not always followed in the reports of their work [illegible] by a good many chemists. It is a matter of good English and good nomenclature. Sentences which may have more than one meaning and names which do not definitely identify compounds are not infrequent in chemical papers. It is the duty of editors to bring about improvements in this respect. It is nevertheless important that those who write papers watch carefully for such situations and correct them; things get past editors.

It is particularly with reference to the names of chemical compounds that improvement is urgent. The journal literature is full of bad nomenclature. May it not rightly be considered the duty of every chemist who writes a paper to attempt to determine the best name for each compound which he has occasion to mention? Unfortunately, this is not always an easy matter, but it is usually possible. For the commoner compounds Webster's New International Dictionary is a good standard. For inorganic compounds Roscoe and Schorlemmer's "Treatise on Chemistry" (Vol. I, The Non-metals; Vol. II, The Metals), and Mellor's "Modern Inorganic Chemistry" are good. The indexes to the *Journal of the Chemical Society* (London) and to *Chemical Abstracts*, in the preparation of which special efforts have been made to keep the nomenclature good, should be helpful. The American Chemical Society's Nomenclature, Spelling and Pronunciation Committee is always willing to do what it can to assist. The chemist especially interested in one branch of chemistry is more likely to fail to use proper nomenclature if he has occasion to enter into the special domain of another branch. For example, it is possible to point out comparatively numerous cases in which a physical chemist has made very exact measurements of some property of an organic compound, giving perhaps a figure involving several decimal places, and then in reporting his results has used a name which is indefinite, as that of a compound with isomers without designation of the particular isomer. The use of good chemical nomenclature is really necessary in the use of good English and in that sense is a cultural attainment. Furthermore, some knowledge of good nomenclature is essential if efficient literature searches are to be made.

Distribution of Literature

The distribution of the journal literature is more or less haphazard and uneven. It is often a problem to lay hands on a needed paper after a reference to it has been located. Desired papers may appear in rare journals available only in a few places and many chemists are located far from good libraries. This situation has been helped greatly in recent years by the introduction in most of the larger scientific libraries of a photostat copying service. Photostat copies of papers can now be obtained from a number of centers at a rate which is approximately equivalent to cost. The significance of this comparatively new facility is apparently not fully recognized as yet and full advantage of it has not been taken. Inter-library lending practice, a translating service by a few libraries, and the lending of rare journals, not available elsewhere, by the office of *Chemical Abstracts*, are other means of obtaining papers.

Many are familiar with the list of current periodicals of interest to the chemist which has been compiled in the office of *Chemical Abstracts*. This list, which now contains well over a thousand entries, is being revised and will soon be published again as a supplement to a number of *Chemical Abstracts*. Announcement is made that, in addition to the customary information as to frequency of appearance, number of volumes per year, price, and publishers' names and addresses, the new list will supply information as to where among the more important libraries of the United States files of the various journals are maintained. Also information will be given in each case as to whether or not a copying, lending, or translating service is maintained by these libraries. Approximately 170 libraries representing all parts of the country will be included. This information on the location of journals has been gathered by the National Research Council. Drs. Harrison E. Howe, Clarence J. West, and Callie Hull deserve credit for providing the instrumentality for effecting this canvass of libraries. With these location data available and photostat service becoming more extensive, the solution of the problem of getting to papers or of obtaining copies should be greatly helped.

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[1] This Journal, 14 [illegible]

Indexes

The main problem, of course, in using the journal literature is in finding references, all that are pertinent to the subject at hand, in order that one may learn what the literature contains and all that it contains relating to this subject. This is often difficult. It is doubtful if there is a more important problem for students, in college or out, to learn how to solve. Its solution involves to some extent a familiarity with the more important journals, particularly the abstract journals, but above all it involves a knowledge of indexes and how to use them. References to the journal literature are often obtained from books or from one paper to others, but mostly they are obtained from indexes, usually of abstract journals. It is frequently assumed that the use of indexes in making literature searches is a simple matter requiring no special experience or ability. This is a mistake. The making of indexes is an art in itself, involving more than a comprehensive knowledge of the general subject being covered, and the use of indexes is no less an art. This deserves emphasis. It is true partly because existing indexes vary greatly in kind, thoroughness, and quality. Even in the use of the best subject indexes the user must meet the indexer part way for really good results. Conscious effort to become a good index user will well repay any scientist. Many a day has been spent in the laboratory seeking information by experiment which might have been obtained in a few minutes, or hours at the most, in the library, had the literature search been efficient. Because of the belief that index searching is a neglected art and yet one of much importance, the remainder of my limited time will be devoted to subject indexes—the most useful kind.

What constitutes a good index? The test is to determine whether or not an index will serve as a reliable means for the location, with a minimum of effort, of every bit of information in the source covered which, according to the indexing basis, that source contains. To meet this test an index must be accurate, complete, sufficiently precise in the information supplied, and so planned and arranged as to be convenient to use. Existing indexes fall far short of this ideal in many cases, and of course somewhat short of it in all cases.

The main purpose in indexing is sometimes partially lost sight of through an effort to bring some sort of classification into it. Classification in connection with indexing frequently detracts from, rather than enhances, the efficiency and usefulness of an index, and is beside the main purpose.

How to Use an Index

The first step in learning how to use subject indexes with maximum effectiveness is to become familiar with the characteristics and peculiarities of important existing chemical indexes. The most significant point to note is whether or not a so-called subject index is really an index of subjects or an index of words. The tendency to index words instead of thoroughly to enter subjects constitutes the greatest weakness in the literature of chemistry. There is a vast difference. Words are of course necessary in the make-up of a subject index, but it is important for an indexer to remember that the words used in the text of a publication are not necessarily the words suitable for index headings or even modifying phrases. Word indexing leads to omissions, scattering, and unnecessary entries. After the most suitable word or group of words from the indexing point of view has been chosen for a heading, it should of course be used consistently no matter what the wording of the text may be. To illustrate a kind of scattering of entries which may result from word indexing, let us consider such a series of article titles as follows:

"An Apparatus for the Determination of Carbon Dioxide," "A New Absorption Apparatus," "Apparatus for Use in the Analysis of Baking Powder," "An Improved Potash Bulb" and "Flue Gas Analysis." Word indexes would no doubt contain an entry under the heading "Carbon dioxide" for the first title, one under "Absorption apparatus" for the second, under "Baking powder" for the third, under "Potash bulb" for the fourth, and one under "Flue gas" for the fifth, and probably no others. These entries seem reasonable enough if the titles are considered separately without thought of the others. And yet the articles may all be descriptive of the same sort of apparatus. As a matter of fact, all these titles might conceivably be used for the same article; if the author happened to be working on baking powder or on flue gas analysis when he conceived the idea for his novel piece of apparatus, or had it in mind particularly for one purpose or the other, he might choose one of the more specific titles for his article rather than one of the more general ones.

In an index entirely based on subjects rather than words, it would be the task of the indexer to see that all these articles get indexed under one heading, or under each of more than one heading, best with cross references pointing from the other possible headings to the one or more headings used. Or, if there seems to be some justification for scattering owing to differences in point of view (word indexing cannot be gotten away from entirely), he would make sure that the necessary cross references are supplied to lead the index user about from heading to heading so that all entries can be readily located. It is not hard to determine whether or not an index is a word index; when this is suspected or noted, one should look around pretty thoroughly in its use instead of being satisfied that the entries found under the obvious heading are all that the index contains on a subject.

It is important to note the approximate degree of completeness of an index in use. There is perhaps no definite point at which a subject index may be said to be complete. The indexing basis is too indefinite. A great many subject indexes are not as full as they ought to be. Aside from word indexing the indexing merely of titles is the most common reason for incompleteness. Titles cannot be depended upon to furnish the information necessary for adequate subject indexing. An index may be reasonably complete from one point of view and not from others. For example, a publication devoted to bacteriology may not reasonably be expected to be indexed fully from the chemical point of view. Completeness in the information supplied in modifying phrases, as well as completeness in index headings, needs to be taken into consideration. It is necessary, of course, to call forth one's resourcefulness to a special degree if a relatively incomplete index is to be used.

Cross references play an important role in subject indexing and in the use of subject indexes. Word indexing is really hard to avoid and cross references are the great preventive. It is a good sign if a subject index has a plentiful supply of cross references, both on the "see" kind and the "see also" kind.[2] They make for uniformity and proper correlation. "See also" cross

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[2] Cross references which refer from a possible heading under which no page references are given to the chosen heading where they may be found are called "see" references, as "Mineral oils. See Petroleum;" those which connect headings representing allied subjects or containing related entries are called "see also" references, as "Iron alloys. See also Steel."

Group of Ohio State University Chemists Who Attended the Pittsburgh Meeting

references are of just as much importance as the "see" kind though not as much used. The service which they render in directing the index user to related headings or to headings which, though dissimilar for the most part, have entries under them likely to be of interest to the investigator who refers to the original heading, is often the chief means of making a search complete. It is not reasonable to expect an index user, or an indexer, as a matter of fact, to think of all of the headings representing related or significant subjects under which headings he may find valuable references that might otherwise be missed. Nevertheless, in the careful indexing year after year of a periodical devoted to a more or less definite field, as an abstract journal for example, subjects are come upon in such a variety of connections and from so many angles that it is possible for a truly comprehensive list of cross references to be built up. The suitability of a given "see also" cross reference may not be clear, much less suggest itself, until a specific case in which it is helpful is observed. It often pays to follow up such a cross reference even when it does not look as if it applies in a given case. The indexer, in surveying the whole field year after year, is in a position to make valuable suggestions in the form of cross references calculated to lead the index user from place to place in the index, so that the chances that his search will be really exhaustive as far as that particular index is concerned are much [illegible]

Persistence is a good qualification for index searching. It is desirable to avoid being too soon satisfied. There is no task in which thoroughness is more important. It involves first a knowledge of the indexing system and of the characteristics of the index. Then one needs to be resourceful, exhausting all possibilities, if he is to avoid some futile searches or incomplete findings. One's fund of general knowledge can usually be [illegible]

On account of the necessity of drawing on one's general knowledge in making a literature search in any field, it is in many instances important that one should make his own searches. It is not always safe to let some one less well informed in a certain field make an index search when a complete survey is desired, even though his familiarity with indexes and the literature in general may be better than one's own. Just as some tasks in the laboratory can be turned over to another to advantage, but not the more important determinations and experiments, so some tasks in the library can be delegated to an assistant, but not all such tasks. Knowledge, skill, and power of observation, are factors fruitful of important results in the library as well as in the laboratory. Literature searching is a dignified pursuit, and it cannot with impunity be assigned to a lower level than that of the laboratory side of problems, as far as the attention it receives is concerned.

With a given problem at hand the first step, of course, is to think out the most likely places to look in the indexes to be used. This may be a simple matter or it may be a very difficult one, depending on the nature of the problem. Difficulty increases with indefiniteness. Experience is necessary. In fact, the beginner is often completely at a loss to know what to do at this very first stage of his search. This point is stressed in the Report of the Subcommittee on Research in Chemical Laboratories, presented to the Committee of One Hundred on Scientific Research, New York, December 26, 1916.[3] In this report, which commends and recommends courses in chemical literature searching in the universities, it is pointed out that the average graduate "fails to analyze the subject" in which he is interested "into its factors, and hence generally looks for topics which are too general. Because he does not find any references to the problem as a whole as he has it in mind, he assumes that nothing has been done upon it and that there is nothing in the literature which will be of aid to him in the investigation. Were he to separate his subject into its essential parts and then to consult the literature on each factor, he would find considerable information which he otherwise would miss." Even though some index headings to which to turn, perhaps the more important ones, may be brought to mind without ingenuity, the completeness of a search may be marred by a failure properly to analyze the problem. Indexes with cross references, particularly "see also" ones, help.

[3] *Science*, **45** (1917), 34.

Too much dependence on cross references is not advisable. They may not be available at all and they are never complete. With a given heading in mind it is well to cudgel one's brain for synonymous words or phrases to try, as well as for variously related subjects, and it is advisable to try these even though entries as expected are found in the first place to which one has turned. Words or phrases with an opposite meaning to the one in mind may serve as subject headings under which desired entries may be found. For example, the searcher interested in viscosity may find significant entries under the heading "Fluidity" in addition to those under "Viscosity." Incidentally, it may be noted that the word "consistency" may serve as a heading for still other related entries. Or, some entries under "Electric resistance" may interest the searcher whose thought on turning to an index was of "Electric conductivity." If such related subjects are not suggested by cross references and have not been thought of in advance, they may be suggested by the nature of some entry under the heading first turned to if one is on the lookout for them.

The resourcefulness required in making a thorough search through subject indexes can best be discussed by treating of an example:

Suppose one were interested in looking up all possible references on vitamins. The first place to which to turn naturally would be the heading "Vitamins" in the indexes to the various reference sources to be used. This would rarely, if ever, be far enough to go. If only one of the indexes contained "see also" cross references, these might be helpful in the use of the other indexes. This playing of one index against another, so to speak, is always a possible means of helping out. Cross references should be looked for. Since it is not always possible to find such cross references and it is not safe to depend too much on them, to be complete one might follow out a line of thought as follows. Vitamins are constituents of foods. It may be worth while to look under "Foods." Entries may be found there with some such a modifying phrase as "accessory constituents of." Vitamins are a factor in health and the effect of foods on health involves the idea of diet or ration. These headings, or this heading if they are combined under "Diet," for example, as would seem best in a true subject index, would no doubt prove fruitful of significant references. Studies of proper diet or of adequate ration for an army would beyond doubt involve the vitamin theory. Experiments to determine the nutritional value of foods are frequently called feeding experiments, so a heading "Feeding experiments" may be looked for to advantage. Food is taken for the purpose of nutrition and the vitamin problem is a nutrition problem. Therefore, the general subject "Nutrition" needs to be examined in the indexes. There is, of course, such a thing as plant nutrition as well as animal nutrition. One might seek to determine, if he did not know, whether or not there is a theory of plant nutrition analogous to the vitamin theory in animal nutrition, so the heading "Plant nutrition" or the heading "Plants" would be suggested. If he did not know it, he would likely learn that there are substances supposed to be factors in plant life, called *auximones* by Bottomley, which are analogous to the vitamins in animal nutrition. The heading "Auximones" would, of course, then be suggested for reference. The lack of vitamins in the diet is considered by some to be the cause of certain diseases (beriberi, pellagra, polyneuritis, scurvy, xerophthalmia). These ought, therefore, to be referred to as index headings. The general heading "Diseases" should be tried also, such a modifying word as "deficiency" being looked for. Perhaps the next thing for the index user to do would be to ask himself, or someone else, whether or not there is a definite name for this general type of disease; he would find that there is and that the name is *avitaminosis*, which should then be turned to as a heading. Certain specific foods have been used and studied, particularly with reference to the vitamin theory—as, for example, polished rice, milk, butter, orange juice, yeast, tomatoes, etc. It seems unreasonable to be expected to think of these, or at least all of them and yet an article entitled, say, "The Effect on Pigeons of Eating Polished Rice," may be word-indexed only in some index, and therefore only get under the headings "Rice" and perhaps "Pigeons." Vitamins have been differentiated as "fat-soluble A," "water-soluble B," etc., and are sometimes spoken of merely in these ways. It is conceivable that some indexes may have these names as headings. In the earlier literature studies resembling the modern vitamin studies are to be found in which other names for the accessory food constituents are used, as nutramines (Abderhalden), bios (Wildiers) and oryzanin (Suzuki). The text referred to from any one of the above mentioned headings may suggest still other headings, as the names of specific foods supposed to be rich in vitamins.

The principle of referring to the general as well as to the specific subject, as exemplified in the preceding paragraph by the subject "avitaminosis" for the general and by the individual deficiency diseases (beriberi, etc.) for the specific, is a good one to keep constantly in mind in using subject indexes. This principle applies aptly in searches for information regarding compounds. Group names for compounds may serve as index headings under which entries of interest to the searcher interested in an individual compound may be found. An example will serve to illustrate:

Supposing one were interested in finding all the information he could with reference to the electrolysis of sodium chloride. In addition to looking up the references under the heading "Sodium chloride" in the indexes to be used, it would be desirable to look also for entries of interest under such headings as the following: "Alkali metal halides," "Chlorides," and "Halides." A process described for the electrolysis of alkali metal halides in general may be of just as much interest and value to the search in hand as one specified to be particularly for sodium chloride, and yet the indexes are not likely to carry entries for each of the members of a group of compounds if a definite group is under discussion. Cross references may be supplied in some cases but it is hardly reasonable to expect an index to go further. A process for electrolyzing chlorides, for instance, could not within reason be entered under headings representing each of the numerous known chlorides. The index user must expect to think of such possibilities and make his search complete accordingly. Another different kind of lead to follow to insure a complete search, particularly when the indexes to be used are word indexes, is to think of the products of the process being studied, in this case chlorine, sodium hydroxide, and possibly sodium hypochlorite. And in addition to looking up the headings represented by the names of these compounds, completeness is insured only by trying the headings "Halogens," "Alkalies," or "Alkali metal hydroxides," and again possibly "Alkali metal hypohalites" and "Hypohalites." The product of some simple electrolytic process which does not involve the recovery of chlorine or alkali may be merely called "bleaching solution" or be given some like name. And still further it may be worth while to look up such a heading as "Potassium chloride" as a representative of a closely related compound which might be subjected to a similar process, or at least might be studied as to the possibilities. Still other headings worthy to be tried are "Electrolytic cells" and possibly "Electrolysis;" this last heading, however, is too general to be used as an index heading for every process involving electrolysis, and is not likely to be used for studies or discussions of specific substances. This whole example serves to show again that resourcefulness and the use of one's general knowledge of chemistry must come prominently into play in the making of index searches.

The resourcefulness necessary in the location of information by means of the great variety of subject indexes in existence may seem to be little more than clever guessing at times. A paper on glass, so called and indexed only under "Glass," may reveal a principle governing the action of metals or other undercooled melts. Authors often fail to see the full significance of their experimental results, and it is not often that the indexer will go further than the author in bringing out this significance for attention. The kind of flexible ingenuity necessary for the location of information in this way is perhaps only to be acquired by experience. It is really more than guessing that results in the location of information in this way, and yet it seems as if a little more than reasoning power, something like intuition, is sometimes necessary.

Chemical publications present a special problem, both to the subject indexer and to the index user, in that many headings must consist of the names of chemical compounds. The difficulties encountered are to be attributed (1) to the fact that many compounds have, or may have, more than one name, (2) the names, or at least the best names, of the more complex compounds may be difficult to ascertain, and (3) new compounds are constantly being prepared, which, if named at all, may receive more than one name which is justified from one point of view or another, and the possibilities of incorrect names are great.

It is not feasible to enter into a detailed discussion of the best procedure in building or using indexes of chemical compounds. The difficulties increase with increasing complexity of compounds. Some indexes are based on systematic nomenclature, irrespective of names used by authors; others are not. Cross references within an index and introductions thereto, and the use by index searchers of dictionaries, chemical encyclopedias, handbooks, and other sources of information leading to a knowledge of the names, sometimes numerous, of compounds, are helps to be utilized. As mentioned above, a knowledge of what constitutes good nomenclature is a great aid in the location of compounds in name indexes. This is particularly important for the organic chemist. It is on account of the almost insurmountable difficulties due to the complexities of chemical nomenclature and because of language differences, that a basis other than their names—namely, their empirical formulas—has been sought and, to a limited extent, used, in the indexing of compounds. A formula index provides a certain means for the location of individual compounds; it is very doubtful if the average chemist can locate compounds in all cases in name indexes even though systematic nomenclature may have been consistently followed in the indexing. In name indexes it is possible, by appropriate devices, to group related compounds to good advantage. This is well brought out in a discussion written in 1919 by Dr. Austin M. Patterson.[4]

The subject index searcher is confronted with nomenclature problems relating to fields other than that of chemical compounds. For example, the chemist interested in plants must contend with the fact that some indexes use the scientific names (genus and species) of plants as headings and others use common names, of which there are frequently several for the same plant.

The use of indexes in foreign languages presents obvious difficulties. It is one thing to be able to read a foreign language and another to translate one's thoughts into that language. The use of an English-French, English-German, or other like dictionary, depending on the language involved, is about the only help available. The introduction to Patterson's German-English Dictionary for Chemists and that to his French-English Dictionary contain some helpful suggestions useful for determining German and French names of chemical compounds.

May I conclude by asking a question? Of the limited amount of information which we as individuals can store in our heads, is it not preëminently desirable that a part of that information consist of a thorough knowledge of where and how to locate additional information when needed?

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[4] THIS JOURNAL, **11** (1919), 989.

Research: Its Position in the Making of an Industry

By John E. Teeple

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FOR THE last three or four years I have been very much interested in three different problems, all in industrial chemistry but in widely separated fields: (1) manufacture of decolorizing carbon, (2) cracking heavy petroleum, (3) manufacture of potash. Although in such widely separated fields, there was a close similarity in the method of handling each one. The ultimate aim in each case was to build a stable industry.

Decolorizing Carbon

In this case the starting point was a process brought to me for investigation. The process proved entirely impractical. The next step was to accumulate some organized facts regarding the importance of various factors in making a good decolorizing carbon, factors such as temperature, pressure, time, raw material, catalyzers, state of division, reaction with gases. On the basis of the facts so gathered, I propounded a working hypothesis to guide the further investigation. The hypothesis was probably wrong in whole or in part, but it served its purpose in directing the work.

We finally succeeded in making on a small scale in the laboratory a better carbon than any commercial product that we could find. The study continued in larger apparatus until the laboratory limit was reached. Then came semiplant scale work, then larger units till the full plant-size unit was reached. Finally, these full-sized units were operated for over a year under most widely varying conditions, until we knew, not only the most favorable methods of operation and treatment on a large scale, but also the proper materials of construction, the shape, size, type, and life of equipment, the allowable limits of control, the proper specifications for a marketable decolorizing carbon, and the proper treatment to meet these specifications. Not until then was a plant finally designed and constructed.

You recognize the method: a persistent study of all factors at each step in increasing the size of the operation, from the smallest laboratory trials to the completed plant. It is slow, but is a very sure way to success. In this case the time was five years from the original discarded impractical process to the full-sized plant, but to-day a plant of over 20 tons per day capacity is in operation making the decolorizing carbon which you know as Darco. This is all that the American industries are educated to using to-day. As their education improves, they will use more, and more plants will be built. This is, in brief, the history of Darco decolorizing carbon from a process which contained no single correct idea to much the largest industry of its kind in America.

Cracking Heavy Petroleum Products

The second problem of cracking heavy petroleum products came to me over four years ago. This was also a process that had passed the laboratory stage, if it ever had one, and was already on a semiplant scale when I first saw it. We succeeded in getting it to operate very, very feebly, so feebly that one had to look twice to be sure it was going, but it seemed to me, after considerable study, to have a basic idea that was right and was possible of commercial development. Having determined this, the next step was to scrap the semicommercial plant and put the operation back into the laboratory to study fundamentals of pressure, temperature, time, character of materials, etc., which should have been done in the first place. From there on its course was the same as the decolorizing carbon. Having learned the respective importance of various factors, it proceeded step by step through the semicommercial-sized unit capable of handling 50 or 60 bbls. per day. To-day it is just going into the last stage of a full-sized unit, and is still probably a year from the design and construction of a full-sized plant. This is the method of cracking oils by using a submerged carbon electrode. It has already been over four years since the process with a right idea in it first came to me for investigation, and in about another year it should be in successful commercial operation.

You recognize the same method as before: A slow and steady trip through the laboratory and semicommercial plants, through full-sized units to the finished industry. Five years in each case. Very slow but very sure.

Now there are many operations that go from an idea to plant practice in much less time, but when it comes to building a new industry or an industry on a new idea it pays to go slow and be thorough and count the time by years—not by days.

This slow progress is usually very aggravating to the inventors and to the people furnishing the money, but I believe it is our duty who are directing such operations to prepare their minds for the long wait, to keep up their interest by intelligent statements of progress, not to allow ourselves to be hurried in any case where results may be prejudiced, and to make them stick to the end. If the people who intend to start such industries have not both the money and the patience to stay by them to the finish, we chemists should discourage them from ever starting.

Manufacture of Potash

The third problem was the manufacture of potash. This came to me something over three years ago as a going plant which was using one process and had a dozen more that had been suggested or partially tried out. But, unfortunately, the process was not turning out very pure or high-grade potash, and the plant was losing money every day. After some study, it seemed to me that there was a fair chance of making an industry here, by following the only method I know—that is, first study the fundamentals in the laboratory. A second problem in this case was by proper engineering and management to make the existing plant operate, if possible—but we are not concerned with that to-day. Our problem here is to approach through the research side.

Now these three problems of decolorizing carbon, cracking petroleum, and making potash, have all been developed, you will see, along exactly the same lines, and through the same method, probably because it is the only method I know by which to make a new chemical industry where one did not exist before. The three problems have taken a large part of my time and attention for three or four years. Two of them are now industries and the third is nearly there, but please do no misunderstand me. *I* did not make these industries. I am not presenting them here as things that *I* have done. There was a time when a man could know all science that was known, and there was another time when a man could know all chemistry that was known, and there probably was a time when *one* man could make an industry. But now, "Them days is gone forever." Making an industry to-day is a many-man job. It requires the coöperation of many minds of different types and training—the research man, the development man, the engineers, the plant managers, control men, business managers, sales managers, financial managers, and money. If any of these are lacking, the industry either is never born or it dies in early infancy. I cannot stress this point too strongly, because I so often meet the chemist who has an idea or a process and who accordingly thinks that he has a whole industry excepting a few minor details. They are not minor details. Often every one of them is more important than his contribution of an idea or a process.

The credit for making industries like these three I have cited must go to the research, development, and control chemists, the engineers, managers, business, financial and sales directors, and the lawyers, who actually do the work. An adviser like myself deserves credit for only three things: first, for the vision to see that an industry is possible; second, for the common sense to see the logical way to develop it and to get the right men working at the right jobs; and third, for the persistence, some might call it obstinancy, that keeps him sticking firmly and unwaveringly to his course and makes him keep everybody else sticking too. He is often a nuisance, but is necessary.

To come back to our potash industry. Then, according to formula, the first job was to throw the whole problem back into the laboratory and gather some fundamental information so that we could know what we were doing in the plant, what we could do, and what we could not do. This should all have been done years before, but never had been.[1]

The plant now has a capacity of 100 tons of potassium chloride a day and about 50 tons of borax. It has not yet quite reached its production in practice, its best output so far being 93 tons of 97 per cent potassium chloride.

It may seem that we jumped from research laboratory to plant practice at 100 tons per day. But not so. In some cases we did actually so jump because the plant was there, was going in bad shape, and if the jump failed no serious damage was done. But I do not recommend building a plant first and experimenting in it afterward. It is altogether too expensive. More often in my hurried sketch I have simply skipped for your benefit the intermediate struggles.

What I have aimed to do here is to emphasize what I believe is the only safe formula for developing an industry—the slow method of fundamentals—and to show you how this has worked out in the potash industry, showing you only the first steps in the research laboratory and the last step in the plant.

Now before I leave this subject, just a word about organization. This plant is in the desert with no civilization near it except of its own making. The company owns the plant, the town, the stores, pipe lines, water lines, railroad, and its part of the lake. The plant manager is a little czar from whom there can ordinarily be no appeal. Sewage, sanitation, housing, feeding, schools, churches, amusements, health, jealousy among wives of employees and small-town scandals, all come to him as the court of last resort. Chemical problems probably occupy the least of his time. Still I tried hard to find a chemically trained man for the position. Of the many men I considered, some I thought would not do for lack of experience or from improper temperament. Of the few who, I thought, might do, some feared to take a chance on the outcome of the proposition, some hesitated to leave present fairly satisfactory positions, some did not want to take their families to the desert, and some simply did not have the nerve or the insides to tackle the job. I finally quit looking for a chemical man and picked a mining engineer from the Michigan School of Mines, not for his training but for his sane judgment and executive ability developed during many years in mining camps in charge of men. Experience cannot be acquired in college or from books. It must be earned. I think we are making a chemist out of him. For plant superintendent the same thing can be said regarding the type of man wanted and failure to find him among chemical men. I finally took a mechanical engineer—a Cornell man with much executive experience. For director of development and research a chemical man had to be found. The man selected is a Columbia chemical engineer. He was chosen not so much because of his actual research ability but on account of his excellence in development work and his executive ability. This man knows the technical operation of the plant better than any of us—a man who can at any time take charge of the plant at a minute's notice and run it for weeks or months.

This is as strictly a chemical plant as there is in America, having no other production than two chemicals. It may seem strange that the best men found for the positions in a chemical plant should be a mining engineer for the manager, a mechanical engineer for superintendent, and a chemical engineer for the head of the research department. Yet the selections have been happy ones, and the results indicate how much more important personality and experience are than training as soon as a man steps outside of the laboratory or has control in any way of other men.

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[1] At this point the author introduced lantern slides illustrating the complexity of the problems encountered and the data incident to their solution. This material will appear later under the authorship of Mr. Harald de Ropp and Mr. W. E. Burke, who did the work.

EIGHTH NATIONAL EXPOSITION OF CHEMICAL INDUSTRIES

Disappointment at the fact that many large, strictly chemical exhibitors have withdrawn in favor of more and more makers of machinery, and speculations as to the future of the Exposition, following a well-defined movement for coöperative management, were the dominant notes in expressions of opinion from visitors at the Eighth National Exposition of Chemical Industries, in the Grand Central Palace, New York, during the week of September 11. Some four hundred exhibitors, largely made up of those who had something to sell the chemical manufacturers, retained for the Exposition its national character, but the absence of many of the chemical exhibitors of previous years was felt by many to have partially nullified its chemical aspect. Meetings of societies and associations in the chemical field, as well as an interesting assortment of addresses and moving pictures dealing with related subjects, added greatly to the interest of the 128,375 visitors in attendance.

The absence of chemical exhibitors lent weight to efforts to revise the plan of the Exposition by making it coöperative. Those fostering this plan believe it possible to bring them into an exposition so operated, and have taken steps to hold a competitive exposition next year on this basis. Just what the outcome will be is difficult to surmise at present, but unquestionably there are a great many supporters for both the present management and the new plan. There are also many exhibitors, however, who incline to the belief that a definite break resulting in two expositions will render both unprofitable from the exhibitors' point of view, and these are planning to await some decision of this point before taking a definite stand on the question. The present management, immediately following the close of the Exposition, stated that in spite of the division the number of contracts already signed for space with them for next year was fully equal to that of previous years.

The exhibits were well arranged and very few failed to show progress in their lines since the previous Exposition. Interest both for technical visitors and for those not acquainted with the details of the industry was held to the fullest extent. Great credit is due those who arranged exhibits for the generally tasteful appearance of the Exposition.

The doors of the Exposition were opened at two o'clock, September 11, by Dr. Chas. H. Herty, president of the Synthetic Organic Chemical Manufacturers Association, and as chairman of the Exposition Committee he presided at the official opening meeting at eight o'clock. Wide interest attached to the address of Wayne B. Wheeler, counsel for the Anti-Saloon League, on the "Attitude of the Anti-Saloon League [illegible] Industrial Alcohol." Other speakers at this session were the Hon. J. M. Wainwright, Acting Secretary of War, Miss Lida Hafford, of the General Federation of Women's Clubs, and Frank H. Riddle, president of the American Ceramic Society.

The Synthetic Organic Chemical Manufacturers Association of the United States met on Tuesday afternoon. The meeting in the conference room on Tuesday evening was addressed [illegible] and Brigadier General Amos A. Fries, of the Chemical Warfare Service. The second annual banquet of the Salesmen's Association of the American Chemical Industry, held Tuesday evening, was addressed by Herbert Hoover, Secretary of Commerce, and by Francis H. Sisson, of the Guaranty Trust Company.

Wednesday was designated as Pulp and Paper Day, and was notable for the session of the Technical Association of the Pulp and Paper Industry, at which representatives of various exhibitors detailed the application of their products to the pulp and paper industry.

Thursday was devoted to the meeting of the Technical Photographic and Microscopical Society, at which the application of photography to technical purposes formed the general subject of a number of informative papers.

The American Ceramic Society met on Friday afternoon, and the New York Section of the American Chemical Society fostered a program on Friday evening which was devoted to standardization in the chemical industry. Notable among the speakers at this meeting was William A. Durgin, of the Department of Commerce, who outlined the accomplishments of the department in the matter of standardization in a wide variety of products and industries in which it has been interested; and Ross C. Purdy, secretary of the American Ceramic Society, who pointed out the virtual impossibility of standardizing refractories on account of the wide variety of uses to which they are put.

On Saturday evening, September 16, at a meeting of the men who went to Washington on August 16 to urge the dye embargo, it was decided to continue for the time being as a loosely knit organization, and to request each plant in the synthetic organic field to appoint a representative to keep in touch with Mr. Pastene, who will maintain touch with the Synthetic Organic Chemical Manufacturers Association, in order that the chemists in these plants shall be kept informed of conditions in their industry and be ready to act on occasion. The suggestion was also made that the AMERICAN CHEMICAL SOCIETY be asked to appoint, through its local sections, men whose duty it shall be to interview and inform each newly elected congressman from that particular territory of the needs and extent of the chemical industry within his district.

Throughout the week, moving pictures dealing with a wide variety of subjects interesting to visitors were shown in a room especially provided for the purpose.

But to return to the exhibits. Probably the most striking feature of these was the absence of four of the five companies, forming the Allied Chemical & Dye Corporation, whose very picturesque booths were the outstanding feature of last year's show. The Barrett Company, occupying a comparatively small and inconspicuous booth, was the sole representative of this group. The du Pont companies were nowhere represented, even by chairs as last year. The Dow Chemical Company and the Sherwin-Williams Company failed to exhibit. These were conspicuous among the absentees.

As last year, the glass blower at the Corning Glass Company booth was a center of attraction. This year he was rivaled by the potter at his wheel in the General Ceramics Company display on the ground floor, who got at the visitors first.

The zinc and copper companies vied with each other in drawing attention to the superior values of their materials for roofing, but at the close of the show no decision was reached.

Of the dye companies only two had exhibits of real interest. Bachmeier & Company had some remarkable specimens of

batik work and artificial flowers. Zinsser & Company presented highly decorative specimens of alizarin print goods and of heavy woolens and hat blanks. The Newport Chemical Works went no farther than decorating a booth in bright colors.

For the first time the U. S. Department of Commerce exhibited, with the idea of drawing attention to its new chemical division and its services to the industry. The Bureau of Chemistry and the Bureau of Mines were both represented.

One of the most interesting exhibits in the entire show was that of the Technical Photographic and Microscopic Society, showing the application of photography—microscopic, color, airplane and motion picture—to technical operations. The airplane map of the City of New York attracted special attention. In this connection the display of optical instruments by the Bausch & Lomb Optical Company was interesting.

It was indeed surprising to find the press room occupying double booth space on the first floor as it was to find the AMERICAN CHEMICAL SOCIETY occupying that generally considered the du Pont space.

The Exposition was well advertised in New York. Even the Fifth Avenue buses carried signs bearing the legend, "Welcome Chemists."

A Yale Idea

At the Sixth Exposition, the Sheffield Scientific School of Yale University initiated an experiment, under the direction of Prof. T. B. Johnson and in the immediate charge of Prof. W. T. Read. The juniors in industrial and engineering chemistry were taken to the Exposition to spend the entire week, attending lectures in the morning and devoting the afternoons to visits at the various booths to study apparatus and machinery used in chemical industry. Upon returning to New Haven the class was given an examination. In the opinion of the Yale authorities, the experiment was so successful that it has been repeated every year since 1920. The students have gained a conception of the construction and operation of chemical apparatus, and have been infinitely benefited by the revelation of the vast scope and power of the chemical industry. The inspiration and vision obtained could not have been gained in any other way.

The success of this plan should encourage other universities and technical schools to make the most of the opportunity which the Exposition affords. There seems to be no reason why small groups from several schools should not combine in providing a very desirable audience, before which the technologists always present at the Exposition could appear and discuss in some detail fundamentals underlying the construction of various types of apparatus to be found in the booths. As Professor Read has suggested, headquarters could be established in a booth devoted to visiting university and college students, where catalogs and trade literature, mounted photographs and drawings, lantern slides and motion picture films, would be found filed under proper classifications so as to be easily accessible. The various exhibits themselves could be cross-indexed in such a way that students might readily find the things they need to see and examine.

A wise choice of experts, whose principal object was instruction rather than sales talk, would give these students a corps of teachers—authorities in their special subjects—which could not be equaled.

Conference on Standardization of Biological Stains

A conference on the standardization of biological stains, at which H. J. Conn presided, was held at the Chemists' Club, New York City, September 16, 1922. The objects of the conference were to arrive at some program whereby the user, the manufacturer and dealer may be benefited. It was the sense of the committee that the user should know when he purchased a stain that it was reliable and for what purposes, and that the stain business be put on a more economical basis, the committee's ability to test stains be placed more directly at the service of the manufacturer, and that plans be formulated for educating the users as to the excellence of American stains and the public as to the importance of this line of business.

The following resolutions were adopted:

(1) That those present lend their support to the continuance of the work of the present committee on standardization.

(2) That, should it be found that the National Research Council does not see its way clear to continue its support, it be recommended that the committee take such independent action as is necessary to carry on its work of standardization and control.

It was further recommended, but without a record vote:

(1) That a list of dyes needed for biological purposes with their Schultz numbers be prepared and that the approximate quantities of each sold be sent to the committee with a view to limiting productive effort to necessary ones only.

(2) That the list of dyes chosen as necessary be published and that standard labels be used on packages in which these dyes are sold.

(3) That these standard labels be given proper publicity by publication.

(4) That the American Society of Bacteriologists arrange for the certification and standardization of such dyes and that they charge a fee for such certification.

More than 90 were present at the dinner of the American Institute of Chemical Engineers at the Pennsylvania Hotel on September 14. It was announced that the Institute now has 550 members and 15 applications. As compared with a $700 balance in the treasury a year ago, there is now $2100 on hand, and there are no outstanding bills. David Wesson, H. C. Parmalee, H. C. V. Dorr, and Maximilian Toch, spoke during the meeting, and a committee, composed of David Wesson, G. W. Thompson, and R. F. Bacon, was appointed to consider the repeal of the New York law governing the registration of chemical engineers.

Richmond, Va., will be the place of the December meeting, the tentative dates being December 11, 12, and 13.

Progress in Inorganic Electrochemistry

By W. G. Horsch

Massachusetts Institute of Technology, Cambridge, Mass.

IN REVIEWING recent progress in inorganic electrochemistry, it seems desirable to include as many topics as possible, touching on each one briefly, and indicating where further information may be found.

W. G. Horsch

The subject of metal recovery will be first considered. Of considerable interest is the well worked-out Ashcroft process for the electrolytic decomposition of anhydrous magnesium chloride employed by the Magnesium Company of Wolverhampton, England,[1] magnesium being first recovered as an alloy with lead, which is subsequently refined electrolytically. Other methods of magnesium recovery have been patented by Seward[2] using a fused fluoride bath, and by Ingeberg.[3] Its recovery from salt-works residue has also been investigated.[4] A brief review of magnesium recovery processes is given by Vickers.[5] Electrolytic zinc apparently has become a permanent industry both in United States and abroad, according to Ingalls,[6] although it is dependent upon large-scale production. It is advocated as an economic proposition in Great Britain.[7] Only a few of the many references can be given. Low cobalt content of the electrolyte is important.[8] One part antimony in two million causes trouble.[9] Several interesting descriptions of plants have been published: Trail, B. C., with a daily capacity of 75 tons;[10] Judge Electrolytic Zinc Plant;[11] and Anaconda.[12] Cadmium is recovered from the bag-house condensation product of copper and lead furnaces, the electrolyte being a pure sulfuric acid leach.[13] Excellent results are claimed for a new cell for producing metallic calcium.[14] Recent patents cover the electrolytic production of sodium from fused sodium chloride[15] and from sodium carbonate in a fused mixture with sodium chloride.[16] Difficulties due to the high vapor pressure of sodium caused the failure of early attempts to use sodium chloride. Electrolysis of fused boric acid, rendered conductive by adding borax, yields boron, a useful metallurgical reducing agent.[17] Patents continue to be issued covering processes for the electrolytic detinning of scrap.[18] Cerium and "misch-metal," obtained by electrolyzing residues from the gas mantle industry, alloyed with iron, produce the pyrophoric alloy used in gas lighters.[19] Other metals that may be deposited electrolytically are chromium,[20] molybdenum[21] and tungsten,[22] the last mentioned being a purification process at 1300° C. The electrolytic recovery of iron from the slime produced by treating iron compounds with caustic alkali has been proposed,[23] also its recovery from waste liquors from the reduction of aromatic nitro compounds,[24] the principal justification being processes demanding a very pure grade of iron.

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[1] [illegible] 38 ([illegible]

[2] U. S. Patent [illegible]

[3] [illegible] Patent [illegible]

[4] Boynton, Lansford and [illegible] 14 (1922), 146.

[5] [illegible] 16 [illegible]

[6] *Trans. Am.* [illegible] 40 [illegible]

[7] Field, *Trans. Faraday Soc.*, **17**, II (1922), 400.

[8] Brit. Patent 126,296 (1919); Clevenger, U. S. Patent 1,283,077.

[9] Hansen, *Mining Met.*, **157**, Sec. 12 (1920), 21.

[10] *Chem. Met. Eng.*, **23** (1920), 227.

[11] Heikes, *Eng. Mining J.*, **110** (1920), 1118.

[12] Laist, *et al.*, *Trans. Am. Inst. Mining Eng.*, **1920**, 1028; *Chem. Met. Eng.*, **25** (1921), 754.

[13] Hanley, *Chem. Met. Eng.*, **23** (1920), 1257.

[14] Brace, *Trans. Am. Electrochem. Soc.*, **37** (1920), 465.

[15] Weaver, U. S. Patent 1,323,936.

[16] Smith and Veazey, U. S. Patent 1,334,179.

[17] Constant and Raisin, Brit. Patent 162,252.

[18] Brit. Patents 122,618, 154,242, and 170,861.

Refining, plating, and electrotyping—processes carried out similarly but differing in purpose—will next be considered. The refining of tin was begun at Perth Amboy in 1916,[25] using a fluosilicate solution later given up in favor of sulfate. A modified fluosilicate solution was recently patented by Mathers.[26] Newman[27] describes a process in which sodium sulfide solution is used. Nickel also may be refined electrolytically.[28]

Electroplating is gradually being removed from a rule-of-thumb to a scientific basis. In the deposition of nickel, Blum[29] has shown that deposits of finer structure and higher tensile strength are obtained from fluoride solutions than from the corresponding chloride solutions. Madsen[30] achieves a similar result by alternately raising and lowering the cathode. Mazuir[31] gives a method for nickel-plating aluminium. Dense adherent deposits of tin are obtained from stannous sulfate solutions containing gelatin.[32] Pyrophosphate baths also are recommended.[33] A novel use for copper is the plating of wooden airplane propellers.[34] Considerable attention has been given lately to zinc plating, which affords better protection than dip galvanizing.[35] Cadmium, plated on iron, successfully resists rusting.[36] Building up the worn parts of machinery by electro-deposited iron has been found practicable.[37] Electrolytic iron has been extensively investigated by Hughes;[38] commercial plant design by McMahon.[39]

In the field of electrotyping, an innovation developed by the Bureau of Standards is the substitution for wax of negatives made by alternately deposited layers of nickel and copper.[40]

Electrolytically formed alloys which have been developed recently are tin-lead[41] and calcium-barium-lead.[42] The science of brass deposition has been extended.[43]

In the field of electrochemical production of chemical compounds many processes have been developed. Some of the following cannot be produced economically under present market conditions, while others are being actively produced on a commercial scale. Anhydrous aluminium chloride,[44] arsenate of lead,[45] chromic acid,[46] ferricyanide,[47] hydrogen peroxide,[48] perborates,[49] perchlorates;[50] perchloric acid by oxidation of hydrochloric acid,[51] permanganate.[52]

Patents are constantly being granted for improvements in the alkali-chlorine industry. These relate mostly to the structural features of cells and diaphragms. A process for recovering bromine from natural brine has been developed.[53] The electrolysis of fused potassium acid fluoride is said to be the best and simplest method known for preparing fluorine.[54] Electrolytic hydrogen and oxygen likewise form a large part of the patent literature. Stimulated by the commercial demand, highly practical cells have been produced.[55]

The phenomenon of cataphoresis has been applied to the purification of clays, to ore concentration, and to the preparation of silica gels from sodium silicate.[56]

Progress has been made in the production of "insoluble" anodes.[57]

Improvements in primary and secondary cells are numerous, but not very striking. A few instances only will be cited. In the indispensable dry cell, the use of porous carbon as a depolarizer has been described.[58] The old problem of the fuel cell is still being studied. A number of cells were tested at temperatures near 800° by Bauer.[59] The combustible materials in the various types were coke dust, carbon rods, hydrogen, and illuminating gas. They are said to possess commercial possibilities. Attempts have been made to reduce nitrogen cathodically to ammonia.[60] The electrolytic fixation of nitrogen as nitric oxide has been patented.[61] A recent development in secondary cells is a very thin plate battery giving much longer life and greater output per unit weight.[62] The theory of the lead cell has been further investigated.[63]

In conclusion it may be stated that whereas electrolysis was originally confined chiefly to electroplating and later extended to refining, it is now taking an increasingly important place in the recovery of metals. As a means of producing chemical compounds, it is often useful but the efficiency in many cases is low. The electrochemist needs improved diaphragms and unattackable anodes which will withstand severe conditions. The development of processes in such a manner as to utilize off-peak power[64] offers many interesting possibilities. The working out of an electrolytic process for iron, using iron ore as a starting point, would be valuable to those localities where iron ore and cheap power are available. The possibilities for research are extensive.

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[19] Hirsch, *Trans. Am. Electrochem. Soc.*, **37** (1920). See also *Brass World*, **16** (1920), 89.

[20] Sargent, *Trans. Am. Electrochem. Soc.*, **37** (1920); Liebreich, Brit. Patent 164,731 (1921).

[21] Förland, U. S. Patent 1,305,350.

[22] Keyes, U. S. Patent 1,293,117.

[23] Estelle, Can. Patent 188,462 (1919).

[24] Kitsee, U. S. Patent 1,298,513.

[25] *Trans. Am. Electrochem. Soc.*, **38** (1920), 163.

[26] U. S. Patent 1,397,222 (1921).

[27] *Z. Elektrochem.*, **27** (1921), 256.

[28] Guess, *Trans. Am. Electrochem. Soc.*, **35** (1919).

[29] *Trans. Am. Electrochem. Soc.*, **39** (1921), 227.

[30] *Ibid.*, **39** (1921), 269.

[31] *Ann. chim. anal. chim. appl.*, **2** (1920), 335; *C. A.*, **15** (1921), 989.

[32] Schlotter, Brit. Patent 148,334 (1920).

[33] Lotterman, *Z. Elektrochem.*, **27** (1922), 573.

[34] Merritt, U. S. Patent 1,335,846.

[35] Wernlund, *Trans. Am. Electrochem. Soc.*, **40** (1921), 345; Horsch and Fuwa, *Ibid.*, **41** (1922), 211.

[36] Knox, *Metal Ind.*, **18** (1920), 556.

[37] MacFadyen, *Engineering*, **108** (1919), 827.

[38] *Trans. Am. Electrochem. Soc.*, **40** (1921); *Electrician*, **86** (1921), 712; *Chem. Met. Eng.*, **26** (1922), 267.

[39] *Chem. Met. Eng.*, **26** (1922), 639.

[40] Blum, *Trans. Am. Electrochem. Soc.*, **40** (1921), 137.

[41] Blum, *Ibid.*, **40** (1921), 147.

[42] Cowan, *et al.*, *Chem. Met. Eng.*, **25** (1921), 1181.

[43] Ferguson and Sturdevant, *Trans. Am. Electrochem. Soc.*, **38** (1920), 87.

[44] U. S. Patent 1,343,662.

[45] Tartar and Grant, THIS JOURNAL, **14** (1922), 311.

[46] McKee and Leo, *Ibid.*, **12** (1920), 16.

[47] Brown, Henke and Miller, *J. Phys. Chem.*, **24** (1920), 230.

[48] Skirrow and Stein, *Trans. Am. Electrochem. Soc.*, **38** (1920), 209.

[49] Alsgaard, *Ibid.*, **40** (1921), 173.

[50] Williams, *Engineering*, **108** (1919), 827; Knibbs and Palfreeman, *Trans. Faraday Soc.*, June **1920**.

[51] Goodwin and Walker, *Chem. Met. Eng.*, **25** (1921), 1093.

[52] *Chem. Met. Eng.*, **21** (1919), 680; THIS JOURNAL, **13** (1921), 763; U. S. Patent 1,377,485.

[53] Dow, U. S. Patent 1,376,610.

[54] Argo, *Trans. Am. Electrochem. Soc.*, **35** (1919), 355; Meyer and Sandow, *Ber.*, **54** (1921), 759.

[55] Barnitz, *Chem. Met. Eng.*, **22** (1920), 201.

[56] Ormandy, *Chem. Age (London)*, **3** (1920), 475.

[57] Fink and Eldridge, *Trans. Am. Electrochem. Soc.*, **40** (1921), 335.

[58] *Compt. rend.*, **172** (1921), 317.

[59] *Z. Elektrochem.*, **27** (1921), 199; *C. A.*, **16** (1922), 206.

[60] Tiede, *Z. Elektrochem.*, **27** (1921), 112.

[61] U. S. Patent 1,376,207.

[62] Hazlett, *Trans. Am. Electrochem. Soc.*, **39** (1921), 89.

[63] MacInnes, *Ibid.*, **37** (1920), 383.

[64] Benson, *Chem. Met. Eng.*, **25** (1921), 1004.

Progress in Organic Electrochemistry

By E. K. Strachan

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THE ELECTROCHEMICAL manufacturers of this country have not, as a rule, been interested in organic chemicals, except as an outlet for some of their by-products, chief of which have been chlorine and hydrogen. The manufacture of monochlorobenzene has reached the proportions of a real industry, and the production of *p*-dichlorobenzene has been stimulated by the discovery of its insecticidal properties, while benzaldehyde and benzoic acid have cut no small figure. Apparently the chlorination of acetylene has never been carried out on any very large scale. The manufacturers of organic chemicals in several instances have turned to electrochemical methods for the recovery of spent reagents, particularly the chromate used for oxidation processes. More than one fair-sized factory has been established on this basis, and promises to survive considerable competition. However, it is the purpose of this review to set forth recent progress in the study of those processes which consist of reaction on an organic material in the electrolytic cell. Very few such are in operation on a factory scale, but those that are give promise of considerable commercial success both for materials requiring tonnage production, and for the manufacture of small quantities of fine chemicals of high purity. But on the whole, the investigation of organic electrochemical methods has proceeded but little beyond the laboratory research stage.

E. K. Strachan

During the period when acetic acid had to be obtained at any cost whatever, thousands of tons of it were made from calcium carbide through acetylene and acetaldehyde. This method cannot compete with wood distillation under present economic conditions, particularly as the makers of pyroligneous acid can throw the burden of competition on their methanol.[1] Nevertheless, this war-time development called attention to the great variety of organic chemicals that can be produced from acetylene.[2] These include aldehyde, paraldehyde, alcohol, acetic acid, ethyl acetate, acetone, ethylene, acetonitrile, pyridine, pyrrole, thiophene, mercaptan, dichloroethane, tetrachloroethane, many other chloro derivatives, chloroacetic acid, crotonic aldehyde, pinacone, isobutyl alcohol, and many other compounds. The shifting of economic conditions and further research may make these reactions of considerable commercial importance: power may be cheaper, motor fuel will undoubtedly increase in price, wood for distillation is apt to be very much scarcer, substitutes or new manufacturing methods may eliminate the strategic importance of methanol. The whole group of materials presents interesting electrochemical possibilities.

Electrochemical methods were applied to this group first for the recovery of the spent mercury catalyst used in the hydration of acetylene. Then it was proposed to make the process continuous by conducting the hydration of the acetylene and recovery of the mercury simultaneously in an electrolytic cell especially devised for the purpose. And finally they were used as an alternative to continue the oxidation until the aldehyde was converted to acetic acid.[3] Other investigations have dealt with the electrolytic oxidation of aldehyde or paraldehyde to acid.[4] Apparently the formation of acid is accelerated by the presence of salts of Mn, Ce, Mo, and V, substances that are known to catalyze other oxidation reactions. The acetic acid may be increased to 40 per cent before it is removed from the electrolyte by distillation. Or, if equivalent alcohol is added before distillation, ethyl acetate is produced.[5] The conversion of acetic acid to acetone is essentially a thermal process, but the reduction of acetone to pinacone may be performed electrolytically,[6] and has received more or less attention. It has been found that the ratio of pinacone to isopropyl alcohol is determined by the electrode material; with electrodes of 90 Pb and 10 Sn, the ratio pinacone: isopropyl alcohol is 10 : 1, while with graphite electrodes the ratio is 6 or 7 : 1. Furthermore, the presence of salts of Bi, Hg, Mn, Ni, Sb, Ag, and Fe tend to reduce the proportion of isopropyl alcohol.

The production of ethyl alcohol from acetaldehyde has received considerable attention.[7] It appears that the concentration of aldehyde must be kept low during the process, never exceeding 10 per cent, and preferably less, to avoid the formation of aldehyde condensation products. By altering the conditions of electrolysis, *e. g.*, raising the temperature, or increasing the aldehyde concentration, polymers and their reduction products, such as crotonic aldehyde, butane -1, 3-, diol, butyl alcohol, etc., may be formed which can serve as denaturants, and thus a denatured alcohol is produced directly from aldehyde.[8]

The reduction of mixtures of aliphatic aldehydes and ketones to diols is described in Brit. Patent 156,145 (1920).

It is interesting to note that in the complete absence of air, aldehyde may be catalytically reduced to ether, although apparently no one has ever done this electrolytically.[9]

There has been interesting progress in the reduction of ω,ω-dibasic acids.[10] The type reaction

$$2NaOOC - X - COOC_2H_5 = 2\overset{+}{Na} + 2CO_2 + \begin{array}{l} X - COOC_2H_5 \\ | \\ X - COOC_2H_5 \end{array}$$

in which $X = CH_2$ has been repeated until a C_{18} acid has been prepared from sodium ethyl malonate. The next step, which would result in the formation of a C_{34} acid, was unsuccessful, probably on account of the soapy and colloidal character of the products. This method has not been applied to aromatic compounds, but work is promised in the near future. The same type of reaction has been proposed as a starting point for the synthesis of tropine derivatives, the basic substances of the atropine, cocaine, and scopolamine groups of alkaloids.[11] It affords an excellent example of the use of electrochemical methods for the production of fine chemicals, a field of manufacture for which they are particularly well adapted. The potassium ethyl ester of acetone dicarboxylic acid, which can be prepared from citric acid, is reduced electrolytically and condenses with itself to succinyl diacetic diethyl ester. The latter substance can be condensed with methyl amine to form *N*-methyl pyrrole diacetic diethyl ester, which in turn can be transformed to tropinone.

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[1] [illegible] 40 [illegible]

[2] [illegible] 6 [illegible] 41 (1921) [illegible]

[3] Brit. Patents 143,891 and 156,147 (1920).

[4] Brit. Patent 124,195 (1919).

[5] Brit. Patent 131,600 (1919). For ethyl acetate see also Brit. Patent 140,115 (1918).

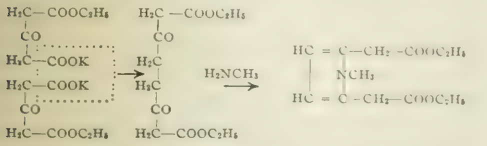
[6] D. R. P. 324,920; 306,304; 324,919 (1917).

[7] D. R. P. 328,342; Brit. Patent 140,115 (1918).

[8] Brit. Patents 140,527 (1919); 140,115 (1918).

[9] Brit. Patent 156,145 (1920); D. R. P. 317,589 (1918).

[10] *J. Soc. Chem. Ind.*, **40** (1920), 169R.



By the same method, the potassium ethyl ester of azelaic acid

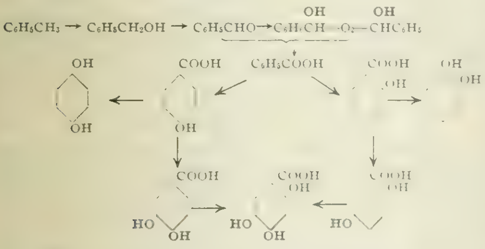
$$KOOC—(CH_2)_7—COOC_2H_5$$

has been converted to

$$C_2H_5OOC—(CH_2)_{14}—COOC_2H,$$

the acid of which proved to be identical with the thapsic acid from juniper berries.[12]

The work of Fichter and his associates deserves especial attention. They have investigated the oxidation of toluene in considerable detail, and find that it proceeds in accordance with the following diagram:[13]



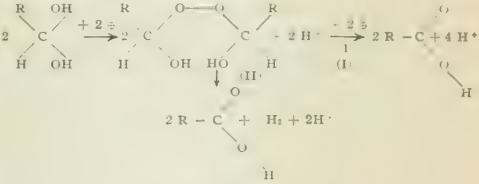
If the various reactions indicated in this diagram can be controlled it suggests interesting possibilities in the production of fine organic chemicals.

The oxidation of dimethylaniline yields tetramethylbenzidine, which is interesting in view of the fact that the analogous reaction with aniline, in which the amino group is unprotected, has never been observed to yield benzidine.[14] The yield is poor, owing to the formation of CO_2, N, CO, and CH_2O, the last of which condenses with the amine. Diethylaniline on the contrary yields almost exclusively tetraethylbenzidine.

A series of exploratory studies[15] is in progress in the same laboratory, one of which[16] shows the formation of *p*-aminophenol from azobenzene. The electrolytic oxidation of azobenzene yields *p,p*-dihydroxyazobenzene, and about twice as much tetrahydroxyazobenzene. This is another illustration of the tendency of organic compounds to oxidize to a greater degree than is desired. Dihydroxyazobenzene of course reduces readily to *p*-aminophenol.

The electrolytic oxidation of naphthalene apparently is similar to that of benzene.[17] Just as the oxidation of benzene does not stop with the formation of phenol or hydroquinone, but proceeds to quinone, so the oxidation of naphthalene yields naphthoquinone as the principal product with traces of α-naphthol, some 1,4-dihydroxynaphthalene, a compound of the quinhydrone type, and phthalic acid.

It was observed sometime ago that, when formaldehyde solution is electrolyzed, equal amounts of hydrogen appear at the anode and cathode for a while, and that then the evolution at the anode gradually ceases. The explanation of this phenomenon constitutes a valuable contribution to the theory of oxidation of aldehydes.[18] The investigator found that by use of a suitable anode constructed of copper coil covered with molten cuprous chloride and reduced electrolytically in alkaline solution the evolution of hydrogen at the anode could be made continuous. The same result is obtained with a similarly constructed silver anode. Moreover, the electrolysis of both acetaldehyde and benzaldehyde exhibits the same phenomenon. The course of the reaction is explained by the following scheme:



The catalytic effect of the electrode causes the intermediate peroxide to decompose by Reaction II with the evolution of hydrogen gas at the anode, while the electrolytic oxidation proceeds by Reaction I. It is quite interesting to compare this with the electrolytic oxidation of methyl and ethyl alcohols which yield, respectively, hydrogen and methane.[19]

Some interesting facts have come to light in a study of the effect of adding various salts to the electrolyte to decrease the cathodic reduction during the electrolysis of chloride to chlorate.[20] In general it appears that the effect of the electrode depends on the system (electrode material–hydrogen–metal deposited from the added salt). Since only small amounts of salt are added—and indeed small amounts of salt appear to be more effective than larger ones—it is probable that the deposited metal does not entirely cover the cathode but merely forms a network on it. Copper deposited on an iron cathode was found to increase reduction, while iron deposited on a copper cathode decreased the reduction to a very small figure. This is strange, since a plain iron cathode reduces much more chlorate than a copper one. The explanation perhaps lies in the capacity of electrolytic iron to occlude hydrogen. These facts should be suggestive to experimenters who are attempting to control the electrochemical oxidation or reduction of an organic material by selection of a suitable electrode. A great deal more work of this sort is needed.

The electrolytic reduction of a number of azo dyes led the investigators to conclude that the rupture always took place at the azo double bond.[21] A suitable small electrolytic cell should therefore be very useful to the analyst of azo dyes, since it would enable him to split dyes of unknown composition into their components without the addition of any foreign material.

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[11] D. R. P. 300,672 (1917).

[12] *Biochem. Z.*, **108** (1920), 75.

[13] Fichter and Uhl, *Helvetica Chim. Acta*, **3** (1920), 22.

[14] Fichter and Rothenberger, *Ibid.*, **5** (1922), 166.

[15] Fichter and Bonhôte, *Ibid.*, **3** (1920), 395; Fichter, Brändlin and Hallauer, *Ibid.*, **3** (1920), 410; Fichter and Schmidt, *Ibid.*, **3** (1920), 704; Fichter and Grissard, *Ibid.*, **4** (1921), 928.

[16] Fichter and Jaeck, *Ibid.*, **4** (1921) 1000.

[17] *J. Chem. Soc. Japan*, **42** (1921), 38; *J. Chem. Soc.*, **120**, I (1921), 334; *J. Chem. Soc. Japan*, **42** (1921), 559; *J. Chem. Soc.*, **120**, I (1921), 726.

[18] Erich Müller, *Ann.*, **420** (1920), 241.

[19] Erich Müller and A. Miro, *Z. Electrochem.*, **27** (1921), 54.

[20] Schlötter, *Ibid.*, **27** (1921), 394.

[21] *Gazz. chim. ital.*, **50** (1920), 149.

Fierz and Wiessenbach[22] report that the reduction of 1,5- and 1,8-nitronaphthalenesulfonic acids, and 1,3,6,8-nitronaphthalenetrisulfonic acid proceeds quite satisfactorily to the corresponding amines. The dye-makers would do well to consider seriously the use of this method of reduction in the factory, since it has much to commend it for the manufacture of H-acid. On the other hand, the reduction of 1,6- and 1,7-nitronaphthalene sulfonic acids produces principally the corresponding hydroxylamines, which rapidly form tarry substances, a statement that sounds quite plausible to anyone who has ever made Cleve acid.

A. Lowy reports the results of a study of the electrolytic oxidation of leucomalachite green.[23]

The role of electrochemistry in the dyeing industry has been discussed by F. Mollwo Perkin.[24]

The possibility of modifying the oxidizing or reducing power of an electrode by altering its potential, and thus exercising control over the products of electrolysis was emphasized by all the early workers in this field who were apparently unaware that the electrode potential is not easy to control, since it is conditioned by the acidity or alkalinity of the electrolyte, and that this in turn frequently affects the course of the reaction more powerfully than the electrode potential does. Furthermore, specific catalytic action of the electrode material is a greater factor in determining the products of electrolysis than over-voltage is. These considerations, coupled with the practical difficulty of producing a reversible electrode of organic material, have resulted in a dearth of information on the single electrode potentials of organic reactions. Two researches have been published recently on this subject, one establishing the potential of the hydroquinone-quinone electrode[25] and the other the oxidizing potential of several anthraquinone-sulfonic acids.[26] It is disappointing that the authors of the latter article did not exercise that care in establishing the identity and purity of their materials for which their laboratory is famous.

No strikingly new features are embodied in recent patents of cells for the electrolysis of organic materials. Several call for a porous electrode through which the organic material may be forced. Others seek to eliminate the diaphragm by employing difference of density to keep the anolyte and catholyte apart, or depend on rotating parts and centrifugal force or an immiscible solvent for this purpose. One particularly interesting looking device allows benzene to rise through the electrolyte to the anode, above which it collects in a layer and is pumped back to the bottom of the cell again. Circulation is maintained until the desired degree of oxidation is accomplished.[27]

The literature on the electrochemistry of organic materials gives the casual reader a sense of a great deal of disorganized effort. Such is partly the case, but in this field, as in many of the newer fields of chemical investigation, a great many exploratory experiments must be performed before investigators can define and limit the problem before them. The experimental work is by no means complete, yet out of the chaos there arise a few guiding generalizations. These, coupled with the knowledge that here and there through the country an organic reaction is being conducted electrolytically on a paying commercial scale, lead to a firm optimism that organic electrochemistry will play a very considerable part in the establishment of America's organic chemical industry.

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[22] *Helv. Chim. Acta*, **3** (1920), 305.

[23] [illegible] **1921** (Preprint).

[24] [illegible] **36** (1920), [illegible].

[25] Biilmann, [illegible] **15** (1921), [illegible]; Sørensen and Linderstrom Lang, *Ibid.*, **16** (1921), [illegible].

[26] Conant, Kahn, Fieser and Kurtz, *J. Am. Chem. Soc.*, **44** (1922), 1382.

[27] U. S. Patent 1,322,580 (1919).

Bibliography of the Grignard Reagent

The National Research Council has recently issued, as Reprint and Circular Series No. 24, a bibliography of the Grignard reagent, entitled "Organomagnesium Compounds in Synthetic Chemistry," by Clarence J. West and Henry Gilman. The first 17 pages comprise a brief discussion of the various types of reaction in which the Grignard reagent may be used. The bibliography proper contains about 1500 references and is arranged alphabetically by author. This is followed by a subject index by compounds, which contains practically all the compounds prepared by means of this very useful reagent.

Up to the present time, interest in the Grignard reaction has been largely scientific. The only apparent reason for this is the fact that the reagent has been considered too unstable for plant use. Recent studies by Gilman indicate that the stability is greater than has been hitherto supposed and this discovery may lead to a more extended industrial use. The wide variety of compounds that can be prepared from this reagent should make it very valuable for the manufacture of research chemicals.

Copies of this work may be obtained from the Publication Division, National Research Council, 1701 Massachusetts Ave., Washington, D. C., for $1.50.

Chicago Chemists Urge Embargo

When the embargo was up in the Senate, fifteen prominent members of the Chicago Section of the AMERICAN CHEMICAL SOCIETY signed the following resolution, which was sent to the senators from Illinois:

> The Chicago Section of the AMERICAN CHEMICAL SOCIETY is thoroughly convinced that a dye embargo is absolutely necessary for proper development of the chemical industries and that it is to the decided advantage of American users of chemicals. Before it is too late, we urge you to reopen the matter and do your utmost in action and support for the embargo.

A. C. S. Monographs

Eight AMERICAN CHEMICAL SOCIETY *Monographs* have been published to date. The first printing of the "Chemistry of Enzyme Action," by Falk, has been exhausted, and it is expected that the accumulation of orders for this volume will warrant a second printing in the near future. Two monographs of the series are now in the hands of the printers and will be published during October, five others are expected to be published during this year, and fifteen are in less advanced stages of preparation. The entire series to date numbers thirty volumes and more will be added from time to time.

Record in Gasoline Production

All previous records for monthly production of gasoline in the United States were broken in July, when 569,711,415 gal. were produced, according to figures compiled by the Bureau of Mines. The increase over July of last year is 150,000,000 gal.

Domestic consumption of gasoline for July was also the largest ever recorded in a single month, amounting to 566,000,000 gal. as compared with 457,000,000 gal. for July of last year. The fact that consumption figures showed a larger increase than the production figures accounts for a reduction of stocks of gasoline for the month, amounting to 52,000,000 gal.

A daily average of 1,593,000 bbl. of oil was run through the stills of 305 refineries reported to the Bureau of Mines as operating during July. This shows an increase of 2.96 per cent in the amount of oil run and a decrease of 5 in the number of operating refineries as compared with June. Plants operating in July ran an average of 89.55 per cent of their daily indicated capacity.

Imports of gasoline for July amounted to 4,840,098 gal., exports were 58,630,402 gal., and shipments to insular possessions were 1,866,789 gal.

Humidity Equilibria of Various Common Substances[1,2]

By Robert E. Wilson[3] and Tyler Fuwa

Research Laboratory of Applied Chemistry, Massachusetts Institute of Technology, Cambridge, Mass.

The following paper is intended to collect for reference, in a single article, data on the humidity equilibria of various common substances.

The paper first discusses the various types of humidity equilibrium curves. Curves are also given for various substances arranged in groups of related materials, as follows: natural textile fibers, artificial textile fibers, pulp and paper fibers, foodstuffs, other organic colloids, absorbents, various forms of carbon, and finely divided inorganic solids.

If the relative humidity is kept constant, there is surprisingly little change in the equilibrium moisture content of most substances over the ordinary range of indoor temperatures. There is need, however, of further work on the effect of temperature changes in connection with hot air drying.

A KNOWLEDGE of humidity equilibria, or the amount of water which is held by various common substances in contact with air of different humidities, is of very considerable importance from a number of different standpoints. The application of such data to problems involving the drying or humidification of materials is obvious. Again, the physical properties of many substances vary greatly, depending upon their precise moisture content. Proper allowances for gain or loss of moisture are also of great importance in buying and selling textiles, etc., where the value per pound is high and it is not desired to pay for unnecessary moisture.

In spite of these and other important applications of humidity equilibria, the data on the subject are, in general, very meager and scattered. The most extensive are undoubtedly those on textiles and paper, but even these are not in satisfactory shape, and there is frequent doubt as to whether the moisture contents are calculated on the dry or moist basis. It has therefore seemed desirable to assemble the most reliable of the available data, to determine experimentally the equilibria for many other common substances, and to present these data in a single article to which reference can readily be made.

It is obvious that in dealing with such materials, most of which are colloidal in nature and not of definite composition, there is no need to seek excessive refinement in the methods, but the values presented are believed to be correct at least within 0.5 per cent moisture for the *particular sample* tested, except for a few cases where special difficulties are mentioned.

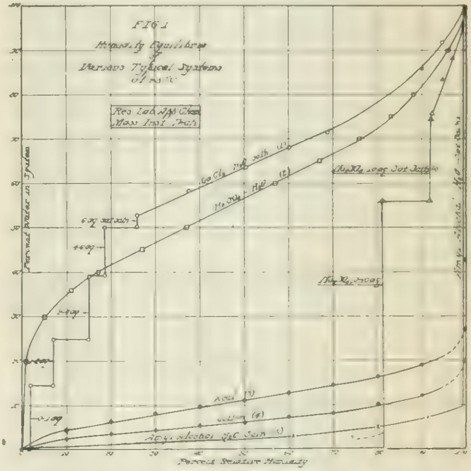
Types of Humidity Equilibrium Curves

Before proceeding to a detailed consideration of specific substances, it may be well to consider briefly the various types of humidity equilibrium curves which are found for different systems. The vapor pressure data for various typical systems are shown in Fig. 1.

Throughout this article, equilibrium vapor pressures are plotted in per cent of that of pure water at the same temperature (25° C.) rather than in millimeters, because the former values change but little with temperature and they represent the "relative humidity" of the air with which they are in equilibrium.

Curve 2, for mixtures of sulfuric acid in water, is a typical vapor pressure curve for a system comprising water and some other liquid which is miscible therewith in all proportions. The very considerable affinity of the acid for the water is clearly shown by the height of the line, especially at very low humidities.

Liquids, such as amyl alcohol, which have much less affinity for water and are only partly miscible therewith, give a different type of curve, shown as No. 5 in Fig. 1. Here, even small amounts of water exert a very high vapor pressure, only 2.2 per cent of dissolved water being in equilibrium with air of 50 per cent relative humidity. The vapor pressure increases somewhat less rapidly up to 9.8 per cent water, which is the limit of solubility of water in isoamyl alcohol. Any additional water then forms increasing amounts of a separate phase containing a small amount of dissolved isoamyl alcohol. The vapor pressure therefore remains constant (vertical line) over a wide range of water contents, until the alcohol phase entirely disappears.



Still a different type of curve is given by the system calcium chloride and water. Solutions of calcium chloride behave very much like those of sulfuric acid, except that the lowering of vapor pressure is somewhat greater, partly due to its lower molecular weight. Eventually a point is reached, however, when the water content drops to 53 per cent, where $CaCl_2.6H_2O$ separates out, giving two phases. From there on, the vapor pressure drops in a stepwise manner, as different pairs of hydrates come into existence. A single hydrate is stable, without changing compositions, over a certain range of vapor pressures, giving a horizontal line. When the next higher hydrate comes into existence the vapor pressure becomes constant while the relative amounts of the two phases change, giving a vertical line.

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[1] Received May 8, 1922.

[2] Published as Contribution No. 52 from the Research Laboratory of Applied Chemistry, Massachusetts Institute of Technology.

[3] Director, Research Laboratory of Applied Chemistry, M. I. T.

It will be noted that, in moderately or very humid air, calcium chloride will take up a greater proportion of its weight of water than sulfuric acid, and hence is, from that standpoint, a better drying agent; but that, for very low humidities, sulfuric acid is markedly superior to calcium chloride. The futility of attempting to get air even 99 per cent dry by the use of calcium chloride is indicated by these curves, although it should be said that they were determined on mixtures of two hydrates and that anhydrous calcium chloride probably *adsorbs* a very small amount of water at vapor pressures lower than the equilibrium pressure of the anhydrous salt plus the monohydrate.

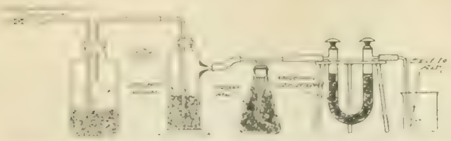
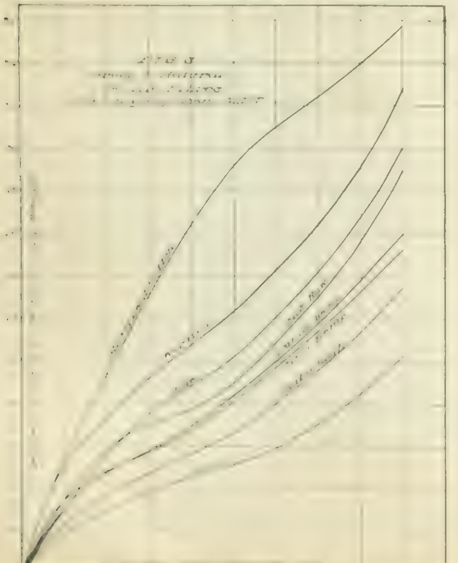


FIG. 2—APPARATUS FOR DETERMINATION OF HUMIDITY EQUILIBRIA

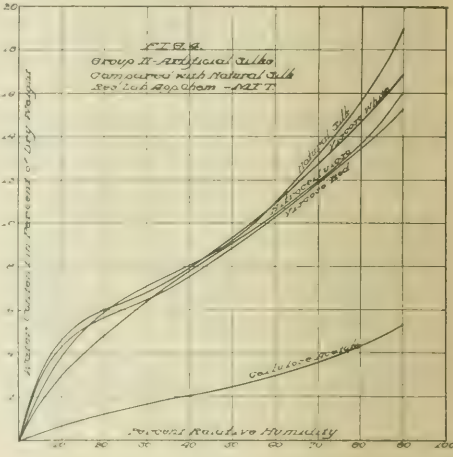
A curve similar in type, but quite different in location, is No. 6, for sodium sulfate and water. Here, the molecular weight is larger and the vapor pressure lowering per unit weight is therefore less in the dilute solution. The decahydrate begins to separate out of the saturated solution at a humidity of over 90 per cent, and even the system decahydrate-anhydrous salt has an equilibrium pressure above 80 per cent. Here, again, there is probably a slight rounding-off of this curve at the lower end, due to adsorption; but in any case, in spite of its high "capacity," the absurdity of using sodium sulfate as a drying agent, except for taking care of liquid water or practically saturated air, is apparent from an inspection of this curve.

A still different type of curve is given by most of the common colloidal substances with which this article is primarily concerned. Clothing, food, structural materials, and finely divided solids tend to take up certain definite amounts of water corresponding to the humidity of the air. Typical curves are those for wool and cotton cloth (Nos. 3 and 4 in Fig. 1). Most textile materials and other organic colloids lie beyond these two limits, and finely divided solids in general still lower than this—in an entirely different range from drying agents such as calcium chloride and sulfuric acid. The vapor pressures of these colloidal materials are, of course, rather variable from sample to sample, as contrasted with the definite reproducible equilibria for hydrates and mixtures of pure liquids.



METHOD USED IN THE DETERMINATIONS

The method used in determining the equilibrium water contents of the substances considered in this article is described in detail in another paper by one of the authors,[4] and therefore a brief description only will be given here.



The substance is subdivided to present a reasonably large surface area, and placed in a weighed U-tube of about 50-cc. capacity. Air, which has been brought to the desired humidity by bubbling through the sulfuric acid bottles, is passed in a slow stream through the U-tube train, as shown by Fig. 2. Moisture equilibrium is generally reached in from 18 to 96 hrs., except in the case of some materials of a colloidal nature, such as soap and gelatin, which are more difficult of equilibration.

Each substance was brought to equilibrium successively in this manner at 15, 30, 50, 70, and 90 per cent relative humidity, after which saturated air was passed through the train for a short time and the same equilibrium points again determined by an approach from the saturated end, *i. e.*, at 90, 70, 50, 30, and 15 per cent relative humidity. Lastly, the dry weight of the sample was found by passing a stream of air, previously dried with phosphorus pentoxide, through the sample, the U-tube being immersed in a bath at about 50° C. This speeds up the approach of equilibrium at the dry end, which is otherwise quite slow, without giving appreciably different results from those obtained by much longer runs at 25° C. In general, these dry weights also check up well with the ordinary "oven-dry" weights at 105° or 110° C., though a few organic colloids give up slightly more water under these conditions.

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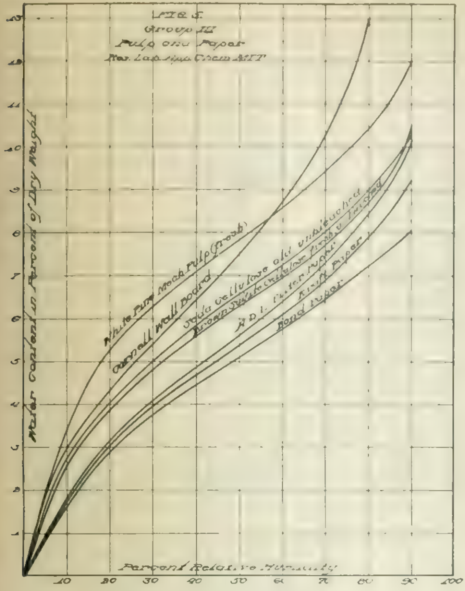
[4] Robert E. Wilson, "Humidity Control by Means of Sulfuric Acid Solutions with Critical Compilation of Vapor Pressure Data," THIS JOURNAL, **13** (1921), 326.



Most of the data presented have been determined in this laboratory, but data from the literature have also been included where they appear to be reasonably reliable. The source of the data for each substance and a brief description of the sample used are given in Table III.

While the data given are believed to be quite accurate for the individual sample tested, most of the materials are colloidal in nature, and the results will undoubtedly vary considerably for different samples of similar material. Indeed, a study of the humidity equilibrium curves is frequently valuable in throwing light on differences in the structure and properties of the same type of material.

The method of calculation of equilibrium moisture is best explained, perhaps, by the use of an actual illustrative example; that of cellulose acetate silk, for instance, is given in Table I.

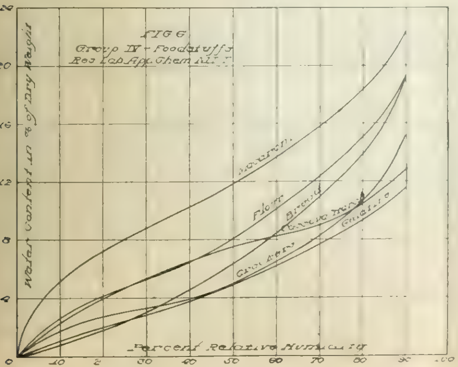
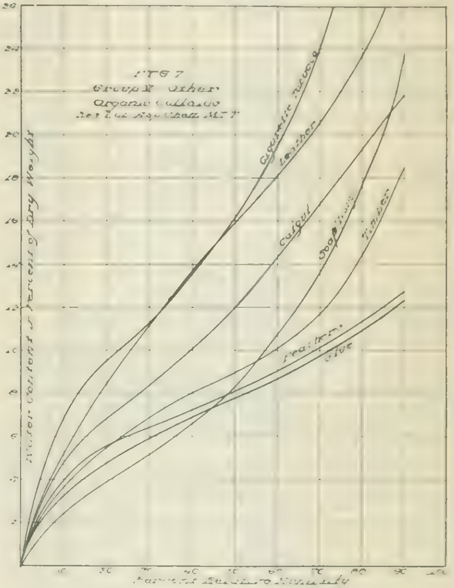


TABLE I—CALCULATION OF EQUILIBRIUM MOISTURE OF CELLULOSE ACETATE SILK

Relative Humidity Per cent	Equilibrium Wt. of Tube and Sample	Equilibrium Weight of Sample	Excess over Dry Weight	Per cent Water on "Dry Basis"	Average of "Up" and "Down" Runs
15	50.5280	6.4243	0.0620	0.97	0.97
30	50.5560	6.4523	0.0900	1.41	1.43
50	50.6200	6.5163	0.1540	2.42	2.44
70	50.6900	6.5863	0.2240	3.52	3.56
90	50.8000	6.6963	0.3340	5.25	5.25
70	50.6953	6.5916	0.2290	3.60	
50	50.6224	6.5187	0.1561	2.46	
30	50.5586	6.4549	0.0923	1.45	
15	50.5275	6.4238	0.0612	0.96	
0	50.4660	6.3623	0.0000	0.00	



RESULTS

The equilibrium moisture for each substance was calculated according to the method of the illustrative example just given. The numerical data recorded in Table III are, however, in practically all cases the mean of the two equilibrium determinations; that is, the up run, and down run made on each sample. In Figs. 3 to 10, these data are presented in graphical form, arranged in several groups of related materials.

It will be noted that, while it is not possible to predict quantitatively the humidity equilibrium curve of a given substance (except in the case of a few pure compounds), a few generalizations can be made in this respect. These may be summarized according to Table II.

TABLE II

PER CENT WATER CONTENTS ON DRY BASIS		
at 50 Per cent Relative Humidity	at 90 Per cent Relative Humidity	NATURE OF SUBSTANCES IN EACH CLASS
0–4	0–6	Finely divided inorganic substances, carbon and lampblacks, coke, rubber, cellulose acetate silk
4–8	8–19	Foodstuffs (except macaroni), paper and pulp fibers, glue, fuller's earth, linen
8–12	13–26	Artificial and natural textile fibers (except cellulose acetate), macaroni, feathers, wood, soap, catgut, ferric hydroxide gel
12–28	22–50	Absorbent cotton, leather, cigarette tobacco, silica gel, activated charcoal

TABLE III—EQUILIBRIUM MOISTURE CONTENTS

		Per cent of Water on Dry Basis					
		Per cent Relative Humidity					
SUBSTANCE	DESCRIPTION OF MATERIAL	15	30	50	70	90	SOURCE OF DATA
Group 1—Natural Textile Fibers							
Absorbent cotton	Sterile absorbent cotton "B & B"	8.9	10.1	20.6	22.2	25.8	Fuwa, R. L. A. C.
Cotton cloth	Sheeting	2.99	4.56	6.7	9.6	13.5	Schloesing[1]
Linen	Table-linen material	2.53	3.60	5.1	7.0	10.2	Atkinson,[2] R. L. A. C.
Jute	Average several grades	4.33	6.9	10.2	14.4	20.2	Storch, R. L. A. C.
Wool	Worsted	6.3	9.0	12.2	17.0	22.9	Schloesing
Raw silk	Cheyennes	5.0	7.1	9.0	13.3	19.0	Schloesing
Sisal hemp	Strands from rope	4.48	5.6	8.3	11.7	15.1	Fuwa, R. L. A. C.
Manila hemp	Strands from rope	4.25	5.6	8.5	11.7	16.0	Fuwa, R. L. A. C.
Group 2—Artificial Textile Fibers							
White viscose silk	Skein of silk	5.6	6.7	9.4	12.9	16.8	Robertson, R. L. A. C
Red viscose silk	Skein of silk	5.3	6.4	9.0	11.8	15.2	
Nitrocellulose silk	Skein of silk	3.95	7.0	9.1	11.8	16.0	
Cellulose acetate silk	Fibrous form	0.97	1.43	2.44	3.56	5.26	
Group 3—Paper and Pulp Fibers							
Mechanical pulp	Pine	4.55	6.3	7.9	9.5	12.0	Müller and Haussner[3]
Sulfite cellulose pulp	Fresh, unbleached	3.35	5.8	6.3	7.8	10.5	
Soda cellulose pulp	Old, unbleached	3.49	5.0	6.6	8.0	10.2	
Kraft paper	60-lb. brown kraft	2.50	3.85	5.4	7.0	9.2	Fuwa, R. L. A. C.
Bond paper	"Manifest" bond	2.34	3.71	5.1	6.5	8.1	
Filter paper	A. D. L. quantitative paper	2.51	4.21	5.6	7.4	10.1	
Cornell wall board	Single-ply, no adhesive	3.71	5.3	7.5	10.3	13.0 (at 80%)	Abrams, R. L. A. C.
Group 4—Foodstuffs							
White bread	Ward Baking Company	0.99	3.14	6.2	11.0	19.0	Atkinson, R. L. A. C.
Crackers	"Uneeda" Biscuit	2.51	3.32	4.98	8.3	14.9	
Macaroni		6.5	8.8	11.7	16.2	22.1	
Flour	Patent	3.55	5.3	7.9	12.3	19.1	Bailey[4]
Starch	Cassava	2.83	5.4	7.6	8.9	12.7	Atkinson, R. L. A. C.
Gelatin		1.01	2.80	4.92	7.6	11.4	
Group 5—Other Organic Colloids							
Leather	Sole leather	7.0	11.1	16.0	20.6	29.2	Phelps[5]
Catgut	Medium grade racquet strings	6.2	8.6	12.0	17.3	21.7	Fuwa, R. L. A. C.
Glue	Best grade hide	4.24	5.8	7.6	10.7	12.5	
Feathers	Pillow down	5.0	6.4	8.1	10.4	12.7	Atkinson, R. L. A. C.
Rubber	Goodyear solid tire	0.17	0.28	0.60	0.74	0.99	Fuwa, R. L. A. C.
Wood (timber)	Forest Products Laboratory. Average	4.65	6.9	9.0	11.5	18.6	Forest Products Lab.
Soap (Ivory)	99.44 per cent pure!	3.36	4.62	8.4	18.4	23.8	Fuwa, R. L. A. C.
Tobacco, cigarette	Fatima cigarettes	8.9	10.1	16.0	24.5	50.1	Lord, R. L. A. C.
Group 6—Absorbents of Various Kinds							
Carbon black	Best quality for rubber trade	2.48	3.42	3.85	4.31	6.0	Fuwa, R. L. A. C.
Ferric hydroxide gel	Made in R. L. A. C.	5.2	6.8	8.1	12.6	20.0	
Silica gel	From Davison Chemical Co.	8.0	12.7	17.3	20.2	22.6	
Soda lime	"Wilson" Brand, 5 per cent NaOH	2.0	3.5	6.5	11.6	24.0	Wilson, R. L. A. C.
Activated charcoal	Coconut charcoal, highly activated with steam	9.5	22.8	28.3	30.0	32.7	Fuwa, R. L. A. C.
Fuller's earth	Florida clay	4.54	...	7.5	...	15.6	
Group 7—Various Forms of Carbon							
Domestic coke	Connellsville coke	0.33	0.60	1.02	1.48	1.89	Selvig and Kaplan[6]
Carbon black	Best grade for rubber trade	2.48	3.42	3.85	4.31	6.0	Fuwa, R. L. A. C.
Activated charcoal	Coconut charcoal, highly steam-activated	9.5	22.8	28.3	30.0	32.7	
Group 8—Finely Divided Inorganic Substances							
Asbestos fiber	Finely divided, organic free	0.22	0.26	0.40	0.62	0.84	Fuwa, R. L. A. C.
Kieselguhr	"Celite"	0.50	0.88	1.40	2.00	3.19	
Zinc oxide	Best grade for rubber trade	0.17	0.29	0.36	0.41	0.59	
Kaolin	Florida	0.30	0.60	0.92	1.06	1.27	
Glass, wool		0.09	0.09	0.17	0.23	0.40	

[1] M. T. Schloesing, Jr., *Bull. soc. encour. ind. nat.*, **1893**.

[2] Mr. Atkinson's results were obtained at Northeastern University under the direction of the writers, and formed the basis of a Bachelor's thesis at that institution

[3] Muller and Haussner, "Der Herstellung und Prüfung des Papiers," p. 1642.

[4] C. H. Bailey, THIS JOURNAL, **12** (1920), 1102.

[5] C. Phelps, M. I. T. Thesis, **1919**.

[6] W. A. Selvig and B. B. Kaplan, THIS JOURNAL, **12** (1920), 783.

It is interesting to note that practically all of the curves have the same general shape, the water content rising comparatively rapidly at low and again at high humidities, and flattening out in the intermediate range between 20 and 60 per cent relative humidity.

Under Group 1, *natural textile fibers* (Fig. 3), it will be noted that wool, jute, and silk have the greatest affinity for moisture, while cotton and especially linen have the least. Absorbent cotton is, however, higher than any of the untreated fibers, presumably as a result of the effect of the severe treatment with alkali, etc., which changes the colloidal properties of the fibers.

The results on Group 2, *artificial textile fibers*, shown in Fig. 4, show a surprisingly close agreement between the equilibrium curves for the viscose and nitrocellulose silks and natural silk. Cellulose acetate, however, holds far less moisture than the others, which accords with its markedly different behavior on dyeing, etc. This should make it possible to use the acetate silk and also cellulose acetate films for certain purposes, where the other cellulose products would not be suitable.

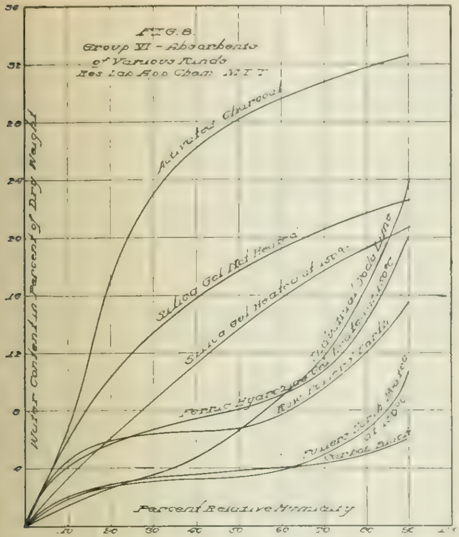
Group 3, covering *pulp and paper fibers* of different types (Fig. 5), shows a very good concordance between the different types of material. The two highest curves are for materials which contain large amounts of lignin (mechanical pulp and wall-board), while the fibers which are primarily pure cellulose check up very well. The kraft and bond papers will, of course, vary, depending upon the amount and nature of sizing and filling materials used.

Group 4, *foodstuffs*, shown in Fig. 6, as a class has a fairly high humidity equilibrium, macaroni being the highest, and flour, starch, bread, and crackers agreeing well among themselves.

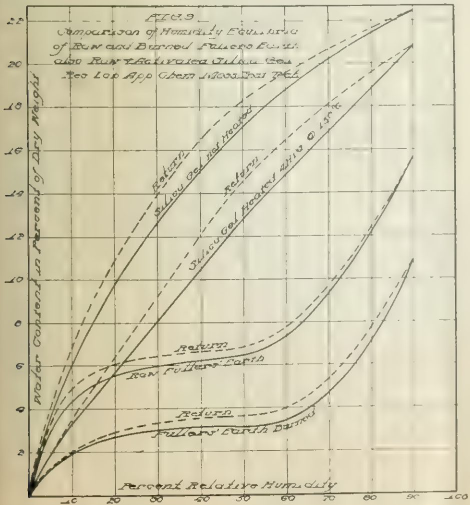
Group 5, *other organic colloids*, shown in Fig. 7, shows the highest humidity equilibria of any class of substances, cigarette tobacco having the highest of any substance studied, and leather the next. The curve for glue is slightly higher than that for gelatin in Fig. 6. Rubber (solid tire stock) is very much lower than any other material in this group, but the equilibrium water content is nevertheless quite appreciable.

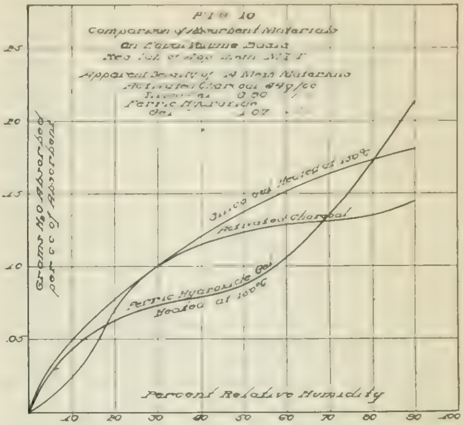
Group 6, covering various types of *absorbents* (Fig. 8), shows a very interesting series of curves with considerable variation in their general shape. Evidently, on a weight basis, activated charcoal holds a far greater amount of moisture than any other absorbent, with unheated silica gel running second.

In the case of silica gel and fuller's earth, the same equilibrium was not readily attained when approached from opposite sides, there being quite a discrepancy between the moisture contents held even after equilibriating for periods as long as 3 or 4 days. This effect is shown clearly in Fig. 9, which shows the values obtained under the two sets of conditions. It also brings out clearly the effect of heating these types of absorbents even to 150°, which makes a marked and apparently permanent change in the amount of moisture which they hold at different humidities.



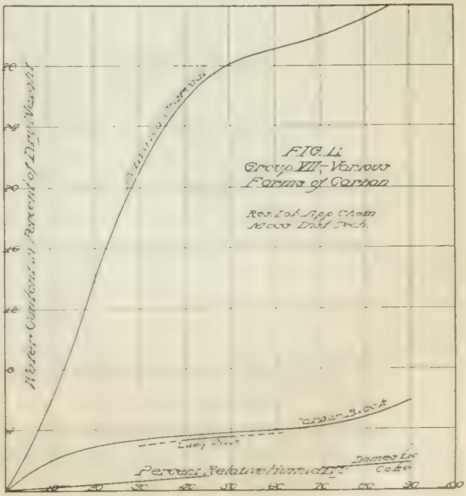
In comparing different absorbent materials, it is frequently the efficiency per unit volume rather than per unit weight which determines their comparative value for many uses. Charcoal, for example, shows up well on a weight basis because of its very low apparent density. By making the comparison on a volume basis, as in Fig. 10, it will be noted that there is a fairly close agreement between the curves for the thrée principal adsorbents, charcoal, silica gel, and ferric hydroxide gel, though their shape is markedly different.



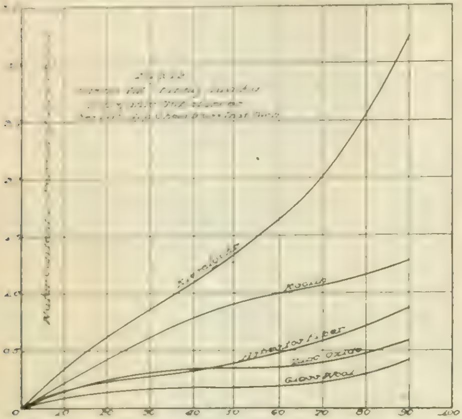


It should also be emphasized that the affinity for water is not a true measure of adsorptive efficiency for other types of gases or vapors and that, in general, silica gel shows up less favorably, and charcoal more favorably, on organic solvents, ferric hydroxide gel having intermediate properties.

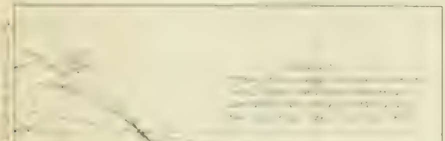
A study of the data for Group 7, *various forms of carbon*, shown in Fig. 11, indicates the enormous difference in the absorptive capacity of a single material, depending upon its state of dispersion. The average individual would assume that carbon black would expose much more surface than activated charcoal and this may be true; but, actually, either its amount or its effectiveness must be much less than that of an equal weight of activated charcoal. Lampblack and carbon black average about the same, though different samples vary considerably.



The *finely divided inorganic solids*, shown in Group 8, Fig. 12, have a characteristically low, but nevertheless definite, absorptive capacity for moisture, kieselguhr being the highest and kaolin the next, as might be expected.



The *effect of temperature* on humidity equilibria is an important question in many cases. It is common experience that heating up air, even for 20° or 30°, makes it a much more efficient drying agent, but this is due primarily to the decrease in its relative humidity rather than directly to the increase in temperature. If the relative humidity is kept constant, there is surprisingly little change in the equilibrium moisture content of most substances over the ordinary range of indoor or outdoor temperatures—an increase in temperature of 25° C. giving a moisture content around 85 per cent of that at the lower temperature. The effect of temperature changes on the equilibrium moisture content at 50 per cent relative humidity is shown in Fig. 13, for a few typical substances on which the data seem fairly reliable. This work should, however, be supplemented before the data are used to work out accurate schedules for hot air drying, etc.



ACKNOWLEDGMENT

In conclusion, the author desires to acknowledge the assistance of the other members of the laboratory staff mentioned in Table III, who have secured much of the foregoing data in connection with their work on other problems.

Chemical Equipment Manufacturers Who Petitioned Congress

The petition to Congress to vote for the amendment extending the Dye and Chemical Control Act, which appeared on page 863 of our September issue, was signed by the following:

Abbe Engineering Co., New York, N. Y.
Abbé, Inc., Paul O., New York, N. Y.
Abernethy, John F., Brooklyn, N. Y.
Ainsworth & Sons, Wm., Denver, Colo.
Air-O-Mix Corporation, New York, N. Y.
Alberger Chemical Machinery Co., Inc., New York, N. Y.
Allbright-Nell Co., The, Chicago, Ill.
Alsing Eng. Co., J. R., New York, N. Y.
Atlas Electric Devices Co., Chicago, Ill.
American Chemical Machinery Co., Chester, Pa.
American Pulverizer Co., St. Louis, Mo.
American Steam Pump Co., Battle Creek, Mich.
American Welding Co., Carbondale, Pa.

Baker & Co., Inc., Newark, N. J.
Baker-Perkins Mfg. Corp., Saginaw, Mich.
Beach-Russ Co., New York, N. Y.
Bethlehem Foundry & Machine Co., Bethlehem, Pa.
Bristol Co., The, Waterbury, Conn.
Brown Instrument Co., The, Philadelphia, Pa.
Burrell Technical Supply Co., Pittsburgh, Pa.

Central Scientific Co., Chicago, Ill.
Chesapeake Copper Smithing Co., Baltimore, Md.
Coors Porcelain Co., Golden, Colo.
Crowell Mfg. Co., Brooklyn, N. Y.
Cruse-Kemper Co., Ambler, Pa.

Devine Co., J. P., Buffalo, N. Y.
Dorr Co., The, New York, N. Y.
Dover Boiler Works, New York, N. Y.
Downington Iron Works, Inc., Downington, Pa.
Duriron Co., Inc., New York, N. Y.
Duro Co., The, Boston, Mass.

Elmore, G. H., Philadelphia, Pa.
Elyria Enameled Products Co., Elyria, Ohio.
Emerson Apparatus Co., Melrose, Mass.
Engelhard, Charles, New York, N. Y.

Fleisher & Co., Inc., W. L., New York, N. Y.
Fletcher Works, Philadelphia, Pa.

General Ceramics Co., New York, N. Y.
General Filtration Co., Inc., Rochester, N. Y.
Giles & Sons, J. S., Chicago, Ill.
Glamorgan Pipe & Foundry Co., Lynchburg, Va.
Goetze Gasket & Packing Co., New Brunswick, N. J.
Greiner Co., The Emil, New York, N. Y.

Hardinge Co., Inc., New York, N. Y.
Harrisburg Pipe & Pipe Bending Co., Harrisburg, Pa.
Hiergesell Bros., Philadelphia, Pa.
Hoskins Manufacturing Co., San Francisco, Calif.
Hubbard's Sons, Norman, Brooklyn, N. Y.
Hydro & Chemical Tank Co., New York, N. Y.

Independent Filter Press Co., Inc., Brooklyn, N. Y
Industrial Filtration Corp., New York, N. Y.

Johnson Co., John, Brooklyn, N. Y.

K-B Pulverizer Co., Inc., New York, N. Y.
Keasbey & Mattison Co., New York, N. Y.
Kelly & Jones Co., The, New York, N. Y.
Kent Machine Works, Brooklyn, N. Y.
Kestner Evaporator Co., Philadelphia, Pa.
Kimble Glass Co., Vineland, N. J.
Knight, Maurice A., East Akron, Ohio.

Lammert & Mann Co., Chicago, Ill.
Lasker Iron Works, Chicago, Ill.
Lippert, F. A., New York, N. Y.
Lyman, Warren M., New York, N. Y.

Mine Safety Appliances Co., Pittsburgh, Pa.
Monarch Mfg. Works, Inc., Philadelphia, Pa.

National Filter Cloth & Weaving Co., Brooklyn, N. Y.
National Pipe Bending Co., The, New Haven, Conn.
Nelson Valve Co., Philadelphia, Pa.
New England Tank & Tower Co., Boston, Mass.
New York Central Iron Works Co., Inc., Hagerstown, Md.
New York Thermometer Co., The, New York, N. Y.

Oliver Continuous Filter Co., San Francisco, Calif.

Parks-Cramer Co., Boston, Mass.
Peterson & Co., Inc., Leonard, Chicago, Ill.

Quigley Furnace Specialties Co., Inc., New York, N. Y.

Ruggles-Coles Engineering Co., New York, N. Y.

Sarco Co., Inc., Buffalo, N. Y.
Scott & Co., Ernest, Fall River, Mass.
Schwartz Sectional System, Indianapolis, Ind.
Shriver & Co., T., Harrison, N. J.
Spencer Lens Co., Buffalo, N. Y.
Sperry & Co., D. R., Batavia, Ill.
Steacy-Schmidt Mfg. Co., York, Pa.
Stokes Machine Co., F. J., Philadelphia, Pa.
Stuart & Peterson Co., Burlington, N. J.
Swenson Evaporator Co., Chicago, Ill.

Thwing Instrument Co., Philadelphia, Pa.
Tolhurst Machine Works, Troy, N. Y.

United Filters Corp., New York, N. Y.
U. S. & Cuban Allied Works Eng. Corp., New York, N. Y.
U. S. Stoneware Co., Akron, Ohio.

Valley Iron Works, Williamsport, Pa.

Western Ref. Tolhurst Machine Works, Troy, N. Y.
Whitlock Coil Pipe Co., Hartford, Conn.

Zaremba Co., Buffalo, N. Y.

The Classification of Coal[1]

By S. W. Parr

University of Illinois, Urbana, Illinois

By use of the ordinary data of proximate analysis, a formula has been developed which gives the true value for the pure coal substance present in all types of coal. "Unit coal" is the term applied to this material to distinguish it from the factors obtained by other formulas which are shown to be in error.

The calorific value for unit coal, because of the direct modification which it undergoes as a result of the oxygen content, is shown to be a good index of rank or type.

A diagram is proposed for indicating rank which makes use of the two characteristic factors, volatile matter and heat value of the unit coal.

Data covering coals from widely separated regions and illustrations of practical application covering an extended period of time seem to establish the status of the method as of possible service to both the investigator and the technician.

SCHEMES for the classification of coal have, in the main, been the outgrowth of technical activities in the countries where they originate, or they may be the formulation of investigational results which reflect the geological or botanical or chemical activities of their authors. A study of the development of methods of classification as an evolutionary process is exceedingly interesting and valuable, but would exceed the limit allowable for a paper of this sort. An accumulation of information, however, is now available which suggests the possibility of formulating a scheme which may serve the needs of both the investigator and technician to an extent which will justify its adoption as a general working proposition. This is a rather ambitious project, it must be admitted, but the end is worth the effort.

Without any question, the most characteristic constituent of a coal is the volatile matter. But if we attempt to make use of that factor simply on a percentage basis, it is at once obvious that it is subject to irregularities resulting from variations in the amount of extraneous matter, even though the coal substance itself remains the same. It becomes evident, therefore, that the use of a percentage value alone develops many inconsistencies.

HISTORICAL

In 1842–43, there was established at the Washington Navy Yard a coal testing plant where more than one hundred and forty steaming tests were made on forty-four different American coals. The results were published in a volume of six hundred pages, but in a manner to be lost to public view. The bibliographic reference in this connection is interesting. It is Senate Document **386** of the 28th Congress, 1st Session, entitled "A Report to the Navy Department of the United States on American Coals Applicable to Steam Navigation and to Other Purposes," by Walter R. Johnson,[2] printed in 1844. This was a monumental piece of work, especially for its time, and while the results have now mainly historic interest, certain methods employed in summarizing the results have had a very pronounced influence on classification.

Professor Johnson had a propensity for reducing his results to relative values with reference to each significant item and tabulating the factors progressively for each item. At the present time, the plotting of a curve would doubtless be the method employed. It is interesting to note, however, that in one of his tables he devotes one column to the ratio of the fixed carbon to the volatile hydrocarbons, $\frac{\text{C}}{\text{V. h-c.}}$, and these ratios are seen to have a certain agreement in their serial order with the "relative evaporation by equal weights of combustible matter." No suggestion is made by Professor Johnson as to the possible use such ratios might serve in general coal classification.

Persifor Frazer, according to a paper read before the Wilkes-Barre (1877) meeting of the American Institute of Mining Engineers,[3] evidently had been seeking for some method of improving upon the scheme of classification proposed by his predecessor, Professor Rogers,[4] who made use of percentage values taken from Johnson's report and elsewhere and referred to the total coal as received. In seeking to eliminate the inconsistencies resulting from wide variation in the ash and moisture, Frazer brought into use the ratio idea of Johnson, arguing that if the fixed carbon and volatile matter were calculated to the ash- and moisture-free basis, the extraneous matter would be excluded. Then, by putting the two values into a ratio, a series of ranking index numbers would result which he proposed to group in a manner to indicate a system of classification. The odd thing about Frazer's discussion is the fact that he seems to think it essential to calculate all values to the pure coal condition so that his two factors for C (fixed carbon) and V. h-c. (volatile hydrocarbons) will equal 100 per cent. Thus,

$$\frac{\text{C}}{1-(\text{ash}+\text{W})} + \frac{\text{V. h-c.}}{1-(\text{ash}+\text{W})} = 100$$

He, therefore, calculated all the analytical data available to the ash- and water-free condition in order to obtain his ratios free from the influence of extraneous or adventitious material. Now a very little inspection will show that this is all wasted energy, since these two values for C and V. h-c. will give the same ratio whether they are taken from the "pure coal" values totaling 100 per cent or from the "as received" values totaling, with the ash and moisture, 100 per cent. His zeal, however, has caused him to err in the right direction; for a ratio, to have any significance, must relate solely to the pure coal substance. Variations from this principle furnish ratios of little or no value. Note in this connection the ratio proposed by Campbell[5] of $\frac{\text{C}}{\text{H}}$, in which H includes all of the hydrogen of the free moisture in the coal, though Strahan and Pollard[6] use the same ratio referred to the dry ashless material.[7]

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[1] Presented before the Division of Industrial and Engineering Chemistry at the 63rd Meeting of the American Chemical Society, Birmingham, Ala., April 3 to 7, 1922.

[2] Walter R. Johnson, Professor of Physics and Chemistry at the University of Pennsylvania, 1839–43.

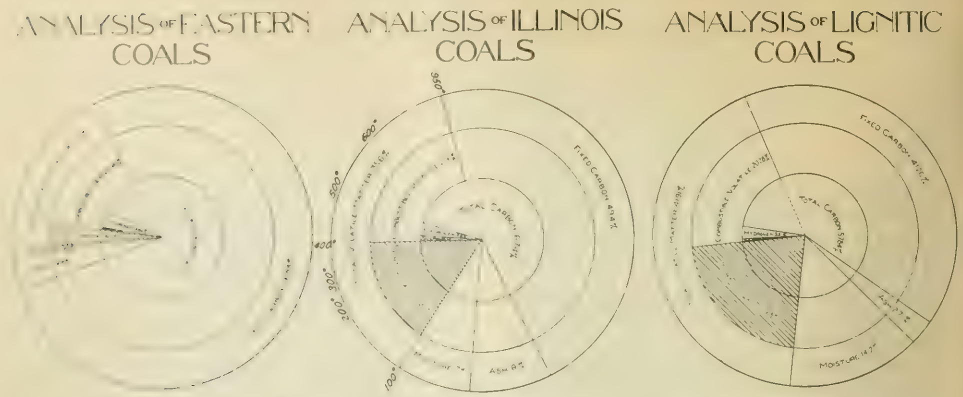
[3] *Trans. Am. Inst. Mining Eng.*, **6** (1877), 430.

[4] H. D. Rogers, "The Geology of Pennsylvania, a Government Report," **2** (1858), 991.

[5] *U. S. Geol. Surv.*, *Professional Paper* **48**, Part I, 156.

[6] "Coals of South Wales," **1915**.

[7] Numerous errors are evident in Frazer's paper; as, for example, his statement that in the data available at that time, the factor for water was included in the volatile matter. All Johnson's data give the moisture values as distinct from the volatile matter.



[illegible]

Average of Ten Illinois Coals Showing Constituents in Relative Proportions

Analysis of a Lignitic or Brown Coal Showing Constituents in Relative Proportions

Fig. 1

In a former system of classification proposed by the author,[8] the ratio employed was $\frac{VC}{C} \times 100$, in which C represented the total carbon and VC that part of the carbon which associates itself with hydrogen to form the volatile hydrocarbons. This ratio is free from inorganic variables and has the advantage with respect to the greater accuracy of obtaining one of the factors, the total carbon. It was recognized in that discussion that another significant element entered into the case which could not be covered conveniently by any ratio. This was the inert part of the volatile matter or oxygen compounds of the coal. In that article, no satisfactory scheme was proposed for taking account of that constituent which we now recognize not only as a part of the true coal substance, but as a very significant factor which, to an equal extent with the volatile matter, determines the rank of a coal.

PROPOSED BASIS OF CLASSIFICATION

As illustrative of a method for taking account of the inert volatile matter, attention is called to the cross-hatched areas in each of the three diagrams in Fig. 1. These areas represent the oxygen compounds of the actual coal substance in each type: (1) a low volatile eastern coal, (2) a high volatile Illinois coal, and (3) a lignitic coal. It is now suggested that the most direct method of classification, and one which would give expression to this constituent, would be the calorific value of the pure coal substance. It should be recognized at the outset, however, that the factors for ash and moisture must not only be very accurately determined, but one disturbing factor, the sulfur, should be eliminated altogether. While a small amount of sulfur is always present in organic form and is a true part of the coal material, the main part, as a rule, is in the form of FeS_2. It is evidently of secondary formation and is so irregular in amount as to indicate the desirability of eliminating it entirely from the actual coal substance. A glance at Fig. 2, showing the organic and pyritic sulfur in different locations in the same mine, is sufficient evidence without further comment as to the desirability of counting the sulfur as part of the extraneous matter.[9]

One other ingredient should be taken account of. In the case of Eastern coals where the ash is low, it has only minor significance, but in lower grade coals, where the ash will average 16 to 18 per cent and may sometimes reach 25 or 30 per cent, it is important. This is the volatile material, chiefly water of hydration, which is discharged at a red heat from the shaley constituents of the ash. With this material assigned to its proper place, along with the sulfur as part of the ash, we are in a position to appreciate the significance of the heat value for the pure coal substance as unaffected by mineral impurities of any sort.

CORRECTION OF FACTORS

This brings us to the method of correcting the factors as determined in the ordinary process of proximate analysis. Fortunately, it resolves itself into a very simple formula. It should be noted that the first description of this formula with a detailed account of its derivation was published in 1909.[10]

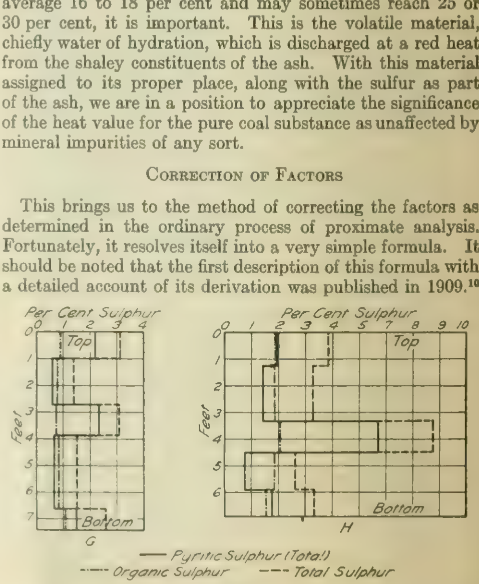


Fig. 2

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[8] S. W. Parr, "The Classification of Coals," J. Am. Chem. Soc., 28 (1906), 1425.

[9] Yancey and Fraser, "The Distribution of the Forms of Sulfur in the Coal Bed," Univ. of Illinois Engineering Expt. Sta., *Bulletin* **125** (coöperative with U. S. Bureau of Mines and Illinois State Geological Survey); THIS JOURNAL, **13** (1921), 35.

[10] Parr and Wheeler, "Unit Coal and the Composition of Coal Ash," Univ. of Illinois Engineering Expt. Sta., *Bulletin* **37**; THIS JOURNAL, **1** (1909), 636.

The application at that time was solely in connection with the calculation of calorific values and had no reference to its use as a classification medium. After long-continued use with all types of coal, the marked accuracy of the formula as first proposed has led inevitably to its use as a classification factor.

It is not necessary to repeat here in detail the derivation of the formula. Its fundamental principles may be readily shown as follows:

Assuming the coal values as derived from analysis to be on the dry basis, then:

$$\text{Non-coal} = \text{Ash as weighed} + {}^5/_8\,\text{S} + 0.08\,(\text{ash} - {}^{10}/_8\,\text{S}) \quad (1)$$

Combining and simplifying, we have Equation 2.

$$\text{Non-coal} = 1.08\ \text{ash} + {}^{21}/_{40}\,\text{S} \quad (2)$$

Hence, to derive the heat value for the unit coal, Equation 3 results.

$$\begin{array}{l}\text{Heat value in}\\ \text{B. t. u. for unit coal}\end{array} = \frac{\text{Indicated B. t. u.} - 5{,}000\ \text{S}}{1.00 - (1.08\ \text{ash} + {}^{22}/_{40}\,\text{S})} \quad (3)$$

In Equation 1, it may be explained that the addition of ${}^5/_8$ S corrects the ash, as weighed, back to the form in which the sulfur was weighed in the original sample, namely FeS_2. The factor in Equation 2 which increases the ash as weighed by 8 per cent is really an arbitrary constant, though it was derived experimentally in the first place by taking the average loss (not including organic matter) on ignition of a number of shales from the Illinois coal measures. It is doubtless mainly water, but may have some carbon dioxide from carbonates, or even sodium chloride, but obviously it should not be applied to the iron pyrites which is shown to be subtracted as Fe_2O_3 from the ash as weighed, the 8 per cent being applied to the remainder only. Equation 3 is derived from Equation 2, by subtracting in the numerator the heat due to the burning of the sulfur and the formation of Fe_2O_3 and in the denominator changing slightly the fraction ${}^{21}/_{40}$ to ${}^{22}/_{40}$, as being in the direction of simplifying the calculation as well as promoting accuracy by compensating slightly for the sulfur not in the pyritic form.

TESTS OF FORMULA

Now while a certain basis in theory may thus be set forth in defense of the formula, it would still be of little value unless it could be proved out in actual use as correct. Several methods suggest themselves. Obviously a coal with high ash from the same mine, or from the same sample by use of the "sink" and "float" method of separation, would respond unfavorably if the 8 per cent constant as applied to the ash were wrong. If this factor is correct, then so far as ash variations are concerned, the B. t. u. values for unit coal should calculate out to substantially the same number. Similarly, the sulfur corrections, when applied to wide variations in sulfur in the same sample or in samples from the same mine, should not produce a divergence in the thermal values when calculated to the unit basis. A great mass of data has accumulated from which only a limited number of illustrations can be given. However, they are typical and cover widely separated localities and practically all types of coal.

Table I is an assembly of results from samples which have been subjected to the "sink" and "float" process. By this procedure, each sample is divided into two parts with widely different values for the ash and sulfur. Manifestly the calculation of the indicated heat value to the corresponding value for the unit coal substance furnishes a crucial test for the suitability of the factors chosen for correcting the ash with reference to water of hydration and for sulfur.

If space permitted, very interesting evidence of an indirect character could be submitted in substantiation of the formula adopted. At least two other methods have been used to a greater or less extent for deriving the pure coal substance. If we compare the results obtained by use of these formulas with the one here proposed, the discrepancies resulting in the case of sink and float samples of the same coal afford positive confirmation of the value of the new formula. A tabulated selection of a few cases only can be given in this connection.

TABLE I—COMPARATIVE VALUES OF PURE OR "UNIT" COAL

					B. t. u.		
		Water	Ash	Sulfur	Actual	Unit Coal	Dif.
1—Grundy	Sink	0.00	21.99	5.00	10,735	14,262	
County, Ill.	Float	0.00	4.57	1.44	13,475	14,217	+45
2—Williamson	Sink	0.00	18.28	1.37	11,731	14,667	
County, Ill.	Float	0.00	4.31	1.07	13,970	14,690	−23
3—Vigo County,	Untrtd.	0.00	16.84	7.62	11,790	14,698	
Ind.	Float	0.00	4.27	3.08	13,870	14,638	+60
4—South Africa	Sink	1.66	18.94	2.28	11,680	15,093	
	Float	1.63	6.06	1.38	13,703	15,065	+28
5—South Africa	Sink	1.82	15.24	1.80	11,847	14,799	
	Float	2.07	8.88	0.87	12,989	14,779	+20
6—South America	Sink	3.59	49.25	2.58	5,922	14,162	
(Brazil)	Float	5.97	17.24	0.68	10,602	14,127	+35
7—Walker							
County, Ala.	Sink	1.00	16.14	0.83	12,467	15,370	
(Pratt seam)	Float	1.20	4.40	0.85	14,384	15,371	− 1
8—Jefferson							
County, Ala.	Sink	0.92	23.70	1.23	11,246	15,620	
(Mary-Lee seam)	Float	1.04	9.78	0.99	13,683	15,576	+44
9—Bituminous	Sink	1.15	4.96	0.76	14,373	15,443	
from W. Va.	Float	1.20	3.40	0.60	14,616	15,416	+27
10—Cannel from	Sink	1.20	39.04	2.87	8,908	16,179	
Kentucky	Float	0.97	13.40	1.74	13,560	16,205	−26
11—Anthracite	Sink	0.70	16.75	1.07	12,280	15,232	
from Pa.	Float	0.86	7.20	0.72	13,795	15,166	+66

TABLE II—COMPARISON OF HEAT VALUES FOR "PURE COAL SUBSTANCE" AS CALCULATED BY THREE METHODS FROM ANALYTICAL DATA ON "DRY COAL"

				Calculated B. t. u.		
	Ash	Sulfur	B. t. u.	*a*	*b*	*c*
Williamson Co., Ill.						
Sink	17.75	1.15	11,766	14,306	14,451	14,608
Float	4.08	0.99	13,924	14,535	14,644	14,623
DIFFERENCE				229	193	15
Franklin Co., Ill.						
Sink	18.00	0.57	11,639	14,194	14,236	14,474
Float	4.64	0.54	13,765	14,436	14,492	14,512
DIFFERENCE				241	256	38
Perry Co., Ill.						
Sink	22.17	1.15	10,922	14,033	14,183	14,413
Float	4.22	0.86	13,763	14,369	14,464	14,452
DIFFERENCE				336	281	39

$$a = \frac{\text{B. t. u.}}{1.00 - \text{A}}; \quad b = \frac{\text{B. t. u.} - 4050\ \text{S}}{1.00 - (\text{A} - \text{S})}; \quad c = \frac{\text{B. t. u.} - 5000\ \text{S}}{1.00 - (1.08\text{A} - {}^{22}/_{40}\,\text{S})}.$$

The derivation of *a*, *b*, and *c* may be understood from the following:

The expression B. t. u. is the indicated heat value, as obtained directly by means of the calorimeter. A is the ash as weighed, and S is the sulfur in per cent.

The method under *a* is the usual one employed by the engineer for determining the heat values for "combustible."

Under *b*, the method employed by Lord and Haas for determining the value of H, *i. e.*, the heat to be credited to the pure coal substance free from moisture, ash, and sulfur.[11]

Under *c*, the formula is that for "unit coal" and has already been discussed.

Note that the analytical values are on the "dry coal" or moisture-free basis. Hence W for water is not introduced into the formulas.

For the reason that a zone of heat values may be indicated or prescribed for groups or types, a method of classification is therefore suggested as a result of the preceding discussion as to the true heat value of the unit coal substance, as shown in Table III.

TABLE III—CLASSIFICATION OF FUEL TYPES BY HEAT VALUES FOR UNIT OR ACTUAL ORGANIC SUBSTANCE

Cellulose and wood	6,500 to 7,800
Peat	7,800 to 11,500
Lignite, brown	11,500 to 13,000
Lignite, black, or sub-bituminous coal	13,000 to 14,000
Bituminous coal (mid-continental field)	14,000 to 15,000
Bituminous coal (eastern field)	15,000 to 16,000
Semianthracite and semibituminous	15,500 to 16,000
Anthracite	15,000 to 15,500

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[11] *Trans. Am. Inst. Mining Eng.*, **27** (1898), 259; also Lord and Somermeier, "Report on Coal," 4th Geol. Surv., Ohio, **1908**, 268.

The groups designated in Table III have been given the names as first proposed by Professor Rogers. These had become sufficiently established at the time of Frazer's paper to make it seem advisable for him to continue their use.[12] Campbell,[13] at a still later date, follows the same general nomenclature and it does not seem wise now to introduce changes in these general and well-established names.

One fundamental criticism has always arisen concerning the use of heat values for designating coal rank. This relates to the lower values for anthracites which bring them into the same class with certain coals of the bituminous type.

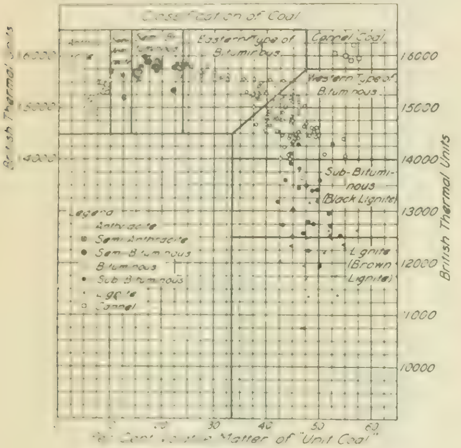

FIG. 3

This feature is really a virtue from the standpoint of the unit coal values as we have been discussing them. How therefore to incorporate this property in a classification scheme has been a problem. It has been solved in a very satisfactory manner by use of a two-dimension diagram, as shown in Fig. 3.[14]

In this chart, the percentage values for unit volatile matter have been located on the horizontal axis and the unit heat values on the vertical. By this means, the low volatile coals of the anthracitic type are segregated from the high volatile coals of the Illinois type even though their heat factors are closely related.

The values in the diagram have been calculated mainly from analytical data published by the U. S. Bureau of Mines.[15] In this way coal samples from widely separated regions are represented.

The dividing lines have been chosen arbitrarily and at even hundreds, but it is interesting to note that for most of the zones there is a marked thinning out of the group representatives at the lines of division. As would be expected, there is more of a blending between the lignites and their neighbors, but in those instances where a sample seems to be out of place it is an even chance that the collector who named the sample was wrong in his diagnosis. At least, the author would hold that the unit B. t. u. is a safer criterion for designating the rank than the physical characteristics which governed the designation at the locality where the samples were taken.

The cannels arrange themselves in a distinct group which reveals at a glance their true characteristics. Similarly, the eastern bituminous of the high volatile type are sharply segregated from the western bituminous as a result of their difference in oxygen or inert volatile content. The names "eastern" and "western" bituminous, however, are not well chosen and should be replaced by names or letters which would be universally applicable.

A word of explanation may be necessary concerning the method of deriving the percentage factor for the unit volatile matter. If we accept the factors as adopted for correcting the ash as weighed, it is seen that the chief constituents entering into those corrections are 8 per cent for the water of hydration of the clayey matter and the addition of $^5/_8$ S to restore the ash to the condition as weighed out in the sample. Now these values are in fact the errors that should be assigned to the volatile matter in the ordinary process of determination, where the 8 per cent of water is driven off at a red heat and approximately $^1/_2$ the sulfur is discharged from FeS_2. The fixed carbon, therefore, has not been appreciably affected, since the errors of the volatile matter naturally appear in the ash as weighed, thus leaving the carbon by difference in substantially its true relationship to the original coal. Hence, to derive the fixed-carbon value on the unit coal basis, we would simply apply the standard formula for deriving the unit coal, thus:

$$\text{Unit fixed carbon} = \frac{\text{Fixed carbon as determined}}{1.00-(1.08\ \text{A} + ^{22}/_{40}\ \text{S})}$$

and from this, by difference:

$$\text{Unit volatile} = 1.00 - \text{unit fixed carbon}$$

TABLE IV

(Calculated to "as received" basis having normal variations of moisture, ash, and sulfur, as indicated. Unit coal: 14,300)

GENERAL LOCATION BY COUNTIES	Coal Bed	Ash	Sulfur	B. t. u. Calculated to Coal "as Received" with 12 Per cent Moisture	B. t. u. Calculated to Coal "as Received" with 14 Per cent Moisture
Sangamon south of Auburn	6	10	4	10,925	10,639
		11	4	10,771	10,484
Perry	6	12	4	10,616	10,330
		13	4	10,462	10,176
Randolph	6	14	4	10,308	10,021
		15	4	10,154	9,867
Clinton	6	16	4	10,000	9,712
		17	4	9,846	9,558
Madison	6	18	4	9,692	9,403
		19	4	9,538	9,250
Montgomery	6	20	4	9,384	9,094

TABLE V—COAL INDEX NUMBERS

		Moisture	Ash	Sulfur	A Unit Coal	B Index No.
1—Anthracite, Scranton, Pa.	Sink	0.70	16.75	1.07	80.62	124.03
	Float	0.86	7.20	0.72	90.96	109.94
2—Bituminous, W. Va.	Sink	1.15	4.96	0.76	93.07	107.45
	Float	1.20	3.40	0.60	94.80	105.48
3—Walker Co., Ala. (Pratt seam)	Sink	1.00	16.14	0.83	81.11	123.29
	Float	1.20	4.40	0.85	93.58	106.86
4—South Africa	Sink	1.82	15.24	1.88	80.73	123.87
	Float	2.07	8.80	0.87	87.86	113.83
5—Brazil, So. America	Sink	3.59	49.25	2.58	41.81	239.17
	Float	5.97	17.24	0.68	75.08	133.26
6—Williamson Co., Ill.	Sink	0.00	18.28	1.37	79.51	125.77
	Float	0.00	4.34	1.07	94.27	105.57
7—Grundy Co., Ill.	Sink	17.28	5.27	2.33	75.48	132.49
	Float	0.00	6.37	2.82	91.57	109.20
8—Vermillion Co., Ill.	Sink	14.45	9.34	2.55	74.06	135.02
	Float	0.00	10.92	2.98	86.57	115.51
9—Franklin Co., Ill.	Sink	9.04	8.56	1.45	80.92	123.57
	Float	0.00	9.41	1.59	88.97	112.39
10—Alberta, Canada C. P. R. Synd.	Sink	1.39	27.50	0.85	68.45	146.09
	Float	1.17	3.02	0.72	95.18	105.06

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[12] [illegible] of his classification, *Am. Inst. Mining Eng.*, [illegible] January 1906, 241.

[13] [illegible] *Paper* 100 A

[14] From an [illegible] for the Master's degree, by E. B. Vliet, University of Illinois, 1918.

[15] Values obtained [illegible] of coals found in *Bur. Mines, Bulls.* **16, 22, 85, 123,** and [illegible] 621

By this means, it will be seen that we have a very definite means of separating the 100 per cent unit coal into its two constituents, fixed carbon and volatile matter, thus fulfilling the preliminary argument that a ratio to be of value must exclude all extraneous matter. These two unit values may be expressed either as a ratio or a percentage, since together they equal 100 per cent, but the percentage values are employed for plotting in diagrammatic form, so as to indicate the comparison to better advantage.

Numerous additional illustrations of the practical value of the unit coal formula and the factors that accompany it might be given. For example, in Table IV, a certain area in Illinois is shown wherein the unit heat value for the coal produced averages 14,300 B. t. u. Assuming certain values for moisture, ash, and sulfur in the coal as marketed, a heat value for a number of average commercial conditions for the coal as delivered has been derived by reversing the calculation, starting from the accepted unit coal value. If the output from any specific mine in that region is known to have a unit coal value of 14,300 B. t. u., the calculated values for the various assumed amounts of impurities will be accurate to within 0.5 per cent of the calorimetric indications, entirely comparable to duplicate results by the same operator on the same sample. Many methods for utilizing such a table or other values deducible by the same formula will readily suggest themselves—such as checking guaranties on coal bids, verifying the samples submitted as to their agreement with the gross shipment, detecting errors in calorimetric results, calculating calorific values in the absence of an instrument, obtaining the variable in heat value for each unit of ash, being exactly 154 units in this particular tabulation, etc.

One other table is submitted as having possible value in matters of every-day concern. In Table V, Column A, are listed the values for the unit coal in per cent of the coal as received. These values are derived simply by application of the unit coal formula incorporating, of course, "W" for the moisture present. Column B gives simply the reciprocal of the values under A and represents the number of pounds of each sample which would be required to furnish 100 lbs. of actual combustible or pure coal substance.

The Electric Steam Generator[1]

By Horace Drever

Electric Furnace Construction Co., 908 Chestnut St., Philadelphia, Pa.

Electric generation of steam has been developed in principle and practice to a definite place in engineering work. Its main features are settled. It has been proved simple, reliable, and safe in daily operation.

It may be profitably utilized in localities where fuel cost is high and hydroelectric power is available on a low firm-power rate.

This device may well be used by central stations to consume their surplus power, and by others who have surplus power under a firm-power contract.

Among the advantages inherent in the electric steam generator are the elimination of fuel transportation, storage, and handling; elimination of ashes, smoke, or dirt; its ready adaptability to the use of surplus power; and its constant readiness for service without large standby losses. It can be located where it is most desirable and requires a minimum of attention. Long pipe lines are unnecessary when this apparatus is used.

A LARGE number of small-capacity units of various types of the electric steam generator have been in use for several years in Europe, where the high cost of fuel and the availability of hydroelectric energy offer extremely favorable conditions for such equipment. The large-capacity units, producing up to 2500 boiler h. p., such as are now in successful operation on this continent, however, are entirely due to the independent development of Mr. F. T. Kaelin, of Montreal.

While the late business depression made available a large surplus of hydroelectric power in many localities and gave cause for the installation of many large units, the actual operation of these units has proved that even where power is available only part of the day, the installation of an electric steam generator may prove a paying investment.

In fact, it is quite likely that users of hydroelectric power who are operating at less than 90 per cent load factor, and who are burning coal for steam purposes, upon investigation will find that a definite saving may be made by the conversion of their off-peak power into steam.

The principles underlying the electric generation of steam are simple and are quite well known, but for a complete exposition of them the reader is referred to a recent paper by F. T. Kaelin.[2] It will be sufficient for the purpose of this short article to recapitulate them here. Steam is generated by passing alternating current directly through the water, which is heated because of its resistance to the current. Usually high-tension power is employed. The amount of heat generated by the passage of 1 kw. hr. of electric energy is equal to 3412 B. t. u. The heat content of 1 lb. of steam at, say, a pressure of 135 lbs. per sq. in., is 1193 B. t. u., and, if we assume a feed-water temperature of 150° F., the total heat to be supplied will be $1193-(150-32)$ or 1075 B. t. u. One kw. hr., will therefore produce 3412/1075, or 3.17 lbs. of steam, no heat loss considered. On large units the heat loss is very small and the thermal efficiency can safely be taken as 98 per cent. On this basis, one kw. hr. will produce 3.10 lbs. of steam.

Under average conditions, 1 lb. of coal of about 12,000 B. t. u. evaporates 8 lbs. of water, and 1 ton, 16,000 lbs. of water. The electric energy required to evaporate the same amount of water is equal to $16{,}000/3.10=5161$ kw. hr. = 215 kw. days = 0.59 kw. yrs. = 0.8 h. p. year. In short, 215 kw. in an electric steam generator are equal to 1 ton of coal per day, burned under average conditions of boiler efficiency. Since the boiler horse power is defined as the evaporation of 34.5 lbs. of water from and at 212° F. per hr. and represents 33,479 B. t. u. per hr., one kw. hr. being 3412 B. t. u. and at an average efficiency of 98 per cent equal to 3344, the relation of b. h. p. to kw. hr. is almost exactly 10 : 1, or an electric steam generator of 1000-kw. capacity is equal to a boiler of 100 b. h. p.

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[1] Received April 5, 1922.

[2] "Generation of Steam by Electricity," *J. Eng. Inst. Canada*, January 19, **1922**; see also F. A. Lidbury and F. A. Stamps, "An Electric Steam Generator for Low Voltage," *Trans. Am. Electrochem. Soc.*, **40** (1921), 77.

Electric steam generators have been built recently in sizes up to 25,000 kw., or 2500 b. h. p. The photographs show several very successful installations. The installation is inexpensive and economical of space. About 100,000 kw. have been installed or are being built for various plants in Canada and the United States.

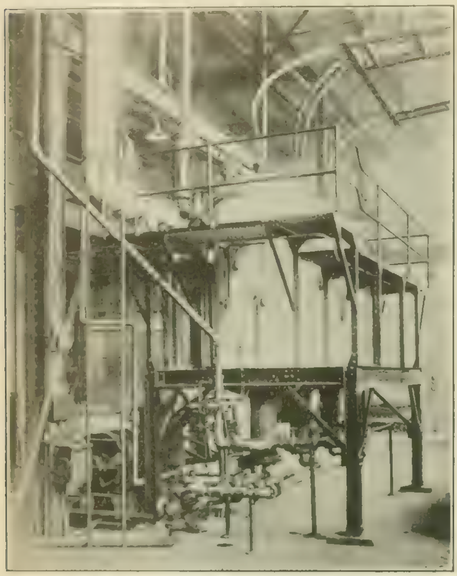

Fig. 1—20,000 Kw.—2000 B. H. P. Electric Steam Generator at Paper Mill

Power supply—6600 volts—3 phase; pressure—135 lbs.

While the electric steam generator is of too recent development to enable us to make an authoritative forecast of its future, we can indicate certain uses and ascertain the outlines of its economic field. European practice applies this type of apparatus to the paper and pulp industries in Scandinavia, where parallel conditions with our northern states and Canada exist; to the chemical and other industries of the Rhone valley and the territory contiguous to the Alpine water powers.

Briefly, wherever abundance of hydroelectric power and high-cost fuel go hand-in-hand, the generation of steam by electricity is probably economical. Such conditions are found in the territories mentioned above and in the western United States, Brazil, Chile, and Japan.

A Temperature Expedient during Periods of Industrial Slackness

The world is passing through a period of subnormal business activity. With demand for their output below the capacity of the plant, many mills are forced to cut costs to the last cent to survive at all. As hydroelectric power bought under a firm rate is usually contracted for in amount to take care of the plant's normal requirements, some of this is being paid for but not used when the mill is running below capacity. If coal is being burned to provide steam for drying or heating while firm power is going to waste, although paid for, the electric steam generator can be installed to use the excess power and save the cost of an equivalent amount of coal. Here it is not a question of the one method being cheaper than the other, but one of saving good dollars and cents that are being paid out when there is already a means at hand to accomplish the purpose, even though the latter is the more expensive method under normal conditions.

Instances are on hand to prove that very often the electric steam generator can pay for itself in a few months and thereafter save the coal bill when conditions are such as outlined in the preceding paragraph. One installation saved its cost in about 2 mo., and is now helping the owner to meet the competitive conditions of the period by the saving it effects in the coal bill.

As an Off-Peak Load

The importance of good load-factor to power stations is undisputed and fundamental. That this is well recognized is shown by the lower rates granted by many central stations for night loads. By installing the electric steam generator to run on off-peak power, week-end power, etc., the load-factor of the system can be boosted, a very favorable rate can be made, and all parties to the contract will be benefited. In this case the steam generator will be used as auxiliary to the existing boiler capacity of the plant. There seems to be a very bright future for such applications in many hydroelectric systems.

As a Replacement of Existing Plant, or as Alternative to New Plant

In the preceding discussion, the generator has been considered without regard to the absolute relative costs of steam produced by the two methods, but under this heading these will be included. Whenever steam is used for any purpose other than power, the fuel-burning boiler can be replaced by the electric steam generator, provided the relations of cost are in favor of the latter. The quality of steam, its pressure, and the amount are exactly the same for both methods, with the one exception that the electric generator does not deliver superheated steam. At first sight it might appear that electric power would have to be extremely cheap and coal very high indeed before serious consideration could be given to the replacement of an installation of coal boilers. On a strictly B. t. u. basis, 1 lb. of coal is equal to about 4 kw. hr., but when the relative efficiencies of application are

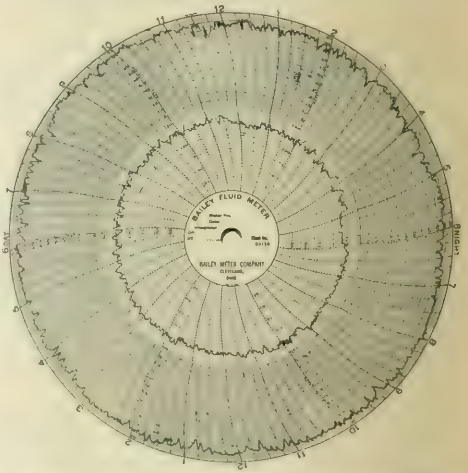

Fig. 2—Bailey Meter Chart from Generator Shown in Fig. 1, Showing Rate of Steam Flow and Pressure

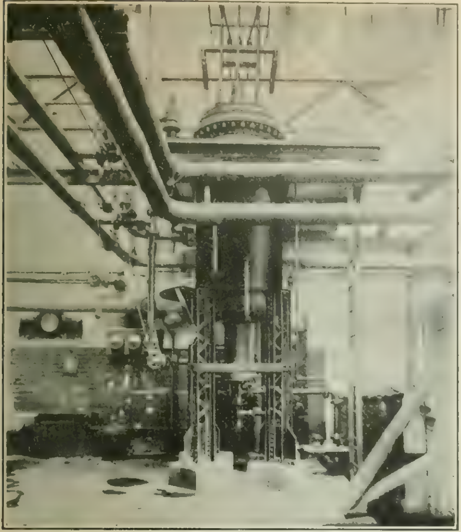

FIG. 3—5000 KW.—500 B. H. P. ELECTRIC STEAM GENERATOR
Power supply—2200 volts—3 phase; pressure—150 lbs.

considered the difference is not so marked. If the average efficiency of small or medium-sized boiler plants is taken as 65 per cent,[3] and that of the electric generator as 98 per cent, we find that 1 lb. of coal of 12,000 B. t. u. is equivalent to $2^1/_3$ kw. hr. Thus, to compete with coal at $10.00 per ton on the cars at the plant, on a basis of fuel cost only, electric power would have to be as cheap as 2 mills per kw. hr. The element of fuel cost is not the only one entering into the problem, however. Labor, interest on investment, and fixed charges generally will be much greater for the coal plant than for the electric generator, and in fact, aside from power cost, every item will be greater for coal plants than for the electric generator. One man can easily do all the work connected with the latter, except major repairs, for units totaling as much as 5000 b. h. p., and where the load is fairly constant, one attendant can operate a plant of twice this size.

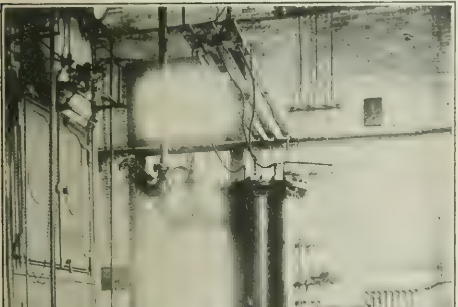

FIG. 4—1300 KW.—130 B. H. P. ELECTRIC STEAM GENERATOR
Power supply—2200 volts—3 phase; pressure—125 lbs.

I—COAL-FIRED PLANT[4]

(a) Cost of plant:	TOTALS
8–400 h. p. stoker-fired boilers—$60[5]	$192,000.00
Buildings and stack	40,000.00
TOTAL INVESTMENT	$232,000.00

(b) Labor:[6] Number of men and duties	No. of Man Hours	Hourly Rate	Total Cost per Day
1 boiler house foreman on shift	24	0.90	$21.60
1 water tender on each shift	24	0.65	15.60
1 foreman of coal handling	9	0.65	5.85
2 coal handlers on each shift	48	0.55	26.40
1 ash handler on each shift	24	0.55	13.20
3 firemen on each shift	72	0.65	46.80
2 helpers on each shift	48	0.55	26.40
	249		$155.85
Yearly cost, 365 days × $155.85			$56,885.25

(c) Fuel cost: At an average boiler and furnace efficiency of 65 per cent, the plant will burn about 60,000 tons of coal per year. Assuming this coal costs $10 per ton in the plant, the annual coal bill will be $600,000.00.

(d) Fixed charges (interest, depreciation, taxes, and insurance) will approximate 14 per cent,[7] or a total yearly charge of $32,480.00.

Combining the various items and making allowances for maintenance and supplies:

Labor	$ 56,885.25
Coal	600,000.00
Fixed charges	32,480.00
Maintenance and supplies (estimated)	6,000.00
TOTAL ANNUAL COST	$695,365.25

Power for operating the coal and ash handling machinery should legitimately be charged against the cost of coal, but no account will be taken of it here.

II—ELECTRIC GENERATOR

(a) Cost of plant including necessary feed pump, hot well, etc.	$41,000.00
Building	12,000.00
	$53,000.00
(b) Labor:	
1 man per shift — 60c—24 man hrs. = $14.40 per day	
Annual labor cost, 365 × 14.40	$ 5,256.00
(c) Power:	
1 b. h. p. requires approximately 13.4 e. h. p. 3200 × 13.4 × $15	$643,200.00
(d) Fixed charges will be taken at 14 per cent of the investment, as in the case of the coal boiler plant 14 per cent × 53,000	$ 7,420.00

Labor	$ 5,256.00
Power	643,200.00
Fixed charges	7,420.00
Maintenance	2,000.00
TOTAL ANNUAL COST	$657,876.00

The saving in favor of the electric generator will be $695,365.25 − $657,876, or $37,489.25, which sum will amortize the plant in less than 2 yrs.

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[3] Fernald and Orrok, "Engineering of Power Plants," p. 158; Henry Kreisinger, "Saving Coal in Boiler Plants," *Universal Eng.*, 1919.

[4] Comparison of a coal-fired boiler installation and an electric steam generator in a typical paper mill. The coal plant will consist of eight 400-h. p. boilers equipped with natural draft stokers and coal and ash handling apparatus. The figures given are assumed to cover an average plant, neither the worst nor the best. Coal will be assumed to cost $10 per ton and electric power $15 per e. h. p. year.

[5] Does not include piping, since this item will be approximately the same for both types of plant.

[6] Loren E. Hibbard, *Tech. Assoc. Papers*, 4th series, p. 19.

[7] Fernald and Orrok, *Loc. cit.*, 255; "Standard Handbook for Electrical Engineers."

The Shatter and Tumbler Tests for Metallurgical Coke[1,2]

By S. P. Kinney[3] and G. St. J. Perrott[4]

SOUTHERN EXPERIMENT STATION, BUREAU OF MINES, TUSCALOOSA, ALABAMA

The Bureau of Mines, in connection with its work on fuels, is conducting at the Southern Experiment Station a study of the physical properties of metallurgical coke in relation to its production and utilization. In connection with this work, a study of present testing methods has been made. This paper describes a series of experiments carried out to determine the best method of procedure and the reproducibility of duplicate determinations with (1) the machine and bag shatter tests, and (2) the tumbler or "hardness" test. Further comparative work is in progress at this laboratory and at coke plants in the district.

The shatter test affords a measure of the relative resistance of cokes to breakage in handling. Single determinations by this procedure contain an average error of 1 to 3 per cent, depending on the character of the coke tested.

It is recommended that several screens be used as indicators of the shattering effect, i. e., 2-in., 1.5-in., 1-in., and 0.5-in.

Results of the bag shatter test are in fair agreement with those of the machine shatter test when the bag is dropped four times.

The effect of the size of the pieces of coke in the sample used for the shatter test upon the absolute and relative value of the results obtained should be further studied.

The tumbler barrel or "hardness" test as at present carried out, i. e., employing 3-in. to 2-in. coke and reporting the result as the percentage remaining on a 0.25-in. screen, has no meaning when the test is applied to cokes of varied physical properties. It may have value as applied to the daily testing of coke supplied to a blast furnace whose coke supply is not subject to large variations in resistance to shattering.

If a screen analysis from 2 in. to 0.25 in. be made after the tumbler test, an indication of the quality of the coke is obtained, but such data indicate no property of the coke which would not be shown by an ordinary shatter test.

If the tumbler test be carried out with 0.75- to 0.25-in. coke, the percentage remaining on a 0.25-in. or 0.17-in. screen after the test is probably indicative of the resistance to abrasion. This value, however, is little different for a variety of cokes and its meaning in terms of blast furnace or other operation is by no means clear.

THE SHATTER TEST

THE SHATTER test is designed to show the resistance of coke to breakage in handling. The method and apparatus, substantially in its present form, were developed some years ago by D. T. Croxton and have been described by Belden.[5] Fig. 1 shows the machine shatter test apparatus in use at this Station. It was built in accordance with tentative specifications formulated by Committee D-6 on Coke, from a blue-print supplied through the courtesy of the Koppers Company.

In the test procedure, a 50-lb. sample of coke is dropped four times from a height of 6 ft. upon a steel plate. The percentage of the original sample, which remains on a 2-in. square mesh screen after this treatment, is reported as the shatter test result.

An alternative method of conducting the shatter test has been proposed by C. R. Meissner of the Koppers Company. In this method the procedure is identical, except that the coke is placed in a heavy sulfate bag about 45 in. long by 28 in. wide and rolled from a shelf 6 ft. above a concrete floor or steel plate. Figs. 2 and 3 show a modification of the bag shatter test used in our work.

Examination of the test procedure shows need for consideration of the following points:

1—Weight of sample to be employed.

2—Method of sampling and size of coke pieces to be taken.

3—Mesh of screen used as indicator of the shattering effect and method of conducting the screening.

4—Agreement obtainable between results of duplicate determinations.

THE TUMBLER BARREL TEST

After the coke is discharged into the bell of the blast furnace it is no longer subject to breakage by impact. The action is then one of slow abrasion as the coke travels down the furnace under the increasing weight of the burden above. A number of workers have developed tests designed to give a relative value for the resistance of coke to mechanical attrition in the furnace. Although there is considerable variation in test procedure, all the methods are the same in principle. A weighed sample of coke is placed in a revolving drum and rotated for a given length of time. Subsequent screen analysis gives a figure said to indicate the friability of the coke, a value not necessarily related to its resistance to shattering by impact.

The first published record of the tumbler test occurs in a paper by Rossigneaux,[6] who states that a revolving drum was used for testing metallurgical coke at Anzin in 1883. According to Simmersbach,[7] drums were used before 1904 for testing coke at Jurjewska, Germany; in Belgium and France similar apparatus containing steel balls was employed. Hewson[8] describes a procedure in which the drum contained steel balls. Cochrane[9] gives data obtained with a similar apparatus containing no steel balls. This author carried out daily tests of the coke used by his furnaces for a number of years and claimed to find a relation between test results and the amount of iron produced by his furnaces and the blast pressure required. The English workers gave the name "hardness" to the property of coke measured by their test.

In this country a similar apparatus has been used for some time by Barrett at Youngstown and by Rice[10] of the Bethlehem Steel Company. A similar "rumbler" test was in use in the Birmingham district some ten years ago. Rice, using

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[1] Presented before the Division of Industrial and Engineering Chemistry at the 63rd Meeting of the American Chemical Society, Birmingham, Ala., April 3 to 7, 1922.

[2] Published with permission of the Director, U. S. Bureau of Mines.

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[4] Associate Physical Chemist, Southern Experiment Station, U. S. Bureau of Mines.

[5] "Metallurgical Coke," *Bur. Mines, Tech. Paper* **50** (1913), 39.

[6] "Propriétés Physiques et Chemique du Coke Metallurgie," *Génie civil*, **20** (1891), 9, 21.

[7] *Stahl u. Eisen*, **33** (1913), 512.

[8] *J. Soc. Chem. Ind.*, **37** (1918), 60.

[9] *J. Iron Steel Inst.*, **97** (1918), 141.

[10] "Importance of Hardness of Blast Furnace Coke," *Am. Inst. Mining Met. Eng.*, Preprint No. 1030 (1921).

an apparatus containing steel balls, found that over a period of months a low hardness number went hand-in-hand with high blast pressure required to blow a given volume of air through the furnace.

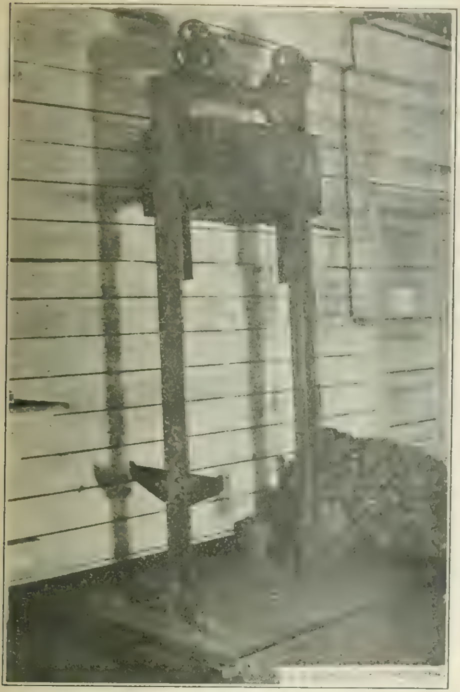

Fig. 1—Machine Shatter Test Apparatus

Drums from 2 to 6 ft. in diameter have been employed, and coke samples of 25 to 900 lbs.

The tumbler test apparatus used at this laboratory is substantially the same as described by Cochrane.[9] The machine, shown in Figs. 4 and 5, consists of a steel drum of 0.25-in. boiler plate, 30 in. in inside diameter and 18 in. in length. The drum is rotated by means of a motor connected to a standard pitch worm gear at the rate of 18.6 r. p. m. The current to the motor is automatically interrupted after the drum has made 1200 revolutions. The machine is set in the top of a bin. The bin discharges on to a set of circular screens 2 ft. in diameter and having the following square openings between wires: 2-in., 1.5-in., 1-in., 0.5-in., and 0.25-in.

A 25-lb. sample of 3- to 2-in. coke is placed in the apparatus for the test, the cover fastened down, and the drum revolved 1200 times. In the subsequent screen analysis, the screens are shaken and the pieces tested separately to see whether they will pass the openings in any position. This procedure gives a more definite end-point than any method of shaking. The so-called hardness number is reported as the cumulative percentage of the original sample remaining on the 0.25-in. screen. As data were desired on the choice of screens to be used for determining the hardness number, a greater number of screens were used than employed by Cochrane.

Examination of the test procedure shows need for consideration of the following points:

1—Weight of sample to be employed.

2—Method of sampling and size of coke pieces to be taken.

3—Mesh of screen used as indicator.

4—Agreement obtainable between results of duplicate determinations.

5—Duration of test.

Coke Samples Tested

The greater part of the work has been carried out on samples of coke from the Birmingham district. Tests have also been made on beehive coke from the Connellsville district, on by-product coke from Benham coal, and on by-product coke from Illinois coal.

Table I—Description of Coke Samples

Name	Type of Oven	Coking Time Hrs.	Coal Seam
Alabama:			
No. 1	Koppers	17	66% Black Creek 34% Mary Lee
No. 2	Beehive	72	Milldale
No. 3	Semet-Solvay	20	Mary Lee
No 4	Beehive	72	Brookwood
No. 5	Semet-Solvay	16	Brookwood & Milldale
No. 6	Beehive	72	Pratt
No. 7	Beehive	72	Mary Lee
No. 8	Semet-Solvay	34	Mary Lee
No. 9	Koppers	19	Pratt
No. 10	Koppers	20	Pratt
No. 11	Beehive	72	Blue Creek
Benham	Wilputte	29	92.5% Keokee 7.5% Pocahontas
Connellsville	Beehive	72	Pittsburgh
Illinois	Roberts	15	No. 7
Pitch coke	Beehive	72	....

Table II—Analysis of Coke Samples

	Proximate				Ultimate					
Coke	Moisture	Volatile	F. C.	Ash	H	C	N	O	S	B. t. u.
Alabama:										
No. 1	1.53	3.17	84.75	10.55	1.42	84.00	1.60	1.52	0.74	12718
No. 2	0.20	0.90	88.57	10.33	0.56	86.79	0.65	0.80	0.85	12624
No. 3	0.18	1.07	84.92	13.83	0.47	83.59	0.72	0.57	....	....
No. 4	0.50	1.35	86.62	11.53	0.53	85.72	0.82	0.47	0.87	12473
No. 5	0.8	1.4	87.10	10.70	0.80	85.0	1.3	1.2	1.0	12690
No. 6	2.39	1.03	85.5	11.06	....	.....	....	....	1.27	12389
No. 7	0.40	0.48	84.37	14.75	....	.....	....	....	0.78	12139
No. 8	3.02	2.92	81.30	12.76	0.70	84.21	1.19	0.88	0.72	12079
No. 9	0.25	1.15	90.70	7.90	0.52	89.16	0.96	0.33	1.11	13044
No. 10	0.50	2.68	87.74	9.08	0.84	87.14	0.74	1.04	1.10	12929
No. 11	0.28	0.57	87.97	11.18	0.31	86.73	0.95	0.00	0.80	12452
Benham	0.9	0.9	91.7	6.5	....	.....	....	....	0.7	13330
Connellsville	0.48	1.77	86.00	11.75	0.79	84.35	1.22	0.86	0.97	12527
Illinois	1.3	1.4	86.0	11.3	0.3	86.2	0.4	0.8	0.9	12450
Pitch coke	0.33	1.07	97.65	0.95	0.55	96.66	0.72	0.62	0.50	14097

Table I shows the character of the coke samples tested. Table II gives proximate and ultimate analyses of the cokes. Table III summarizes data obtained on physical properties of the coke samples. True density was determined on material ground to pass a 200-mesh screen. Apparent density was determined on 1.75-in. material by a method measuring the volume of water displaced by a weighed amount of the coke.

Detailed Data of Machine and Bag Shatter Test Determinations

To determine the agreement obtainable between the results of the machine and bag shatter tests and the agreement obtainable between duplicate determinations by each method, a series of tests was run on two by-product cokes made in Alabama. Part of these tests were carried out at the laboratory and part were run at the plant. Sufficient coke to run from five to ten tests was taken at one time and well mixed on the floor before the shatter tests were made. The purpose of the tests was not so much to get a representative sample of the coke contained in the bin or larry car as to secure a large well-mixed pile of coke from which identical samples might be taken.

TABLE III—PHYSICAL PROPERTIES OF COKE SAMPLES

Coke	Shatter	Hardness A[1]	Hardness B[2]	Specific Gravity True	Specific Gravity Apparent	Porosity
Alabama:						
No. 1	73	70	.	1.75	0.96	45
No. 2	74	75	89.1	2.10	1.02	52
No. 3	[illegible]	75	89.4	1.96	1.00	49
No. 4	72	67	..	1.91	0.83	57
No. 5	[illegible]	71	90.6	2.00	0.99	51
No. 6	[illegible]	74	90.2	2.13	1.15	46
No. 7	72	71	88.8	1.91	0.98	49
No. 8	76	74	90.4	1.98	1.05	47
No. 9	70	74	92.3	2.04	1.14	44
No. 10	70	68	...	1.92	0.98	49
No. 11	77	73		1.97	0.81	59
[illegible]	[illegible]	73	88.4	1.85	0.91	51
[illegible]	[illegible]	71	92.0	1.89	1.02	46
[illegible]	42	78	90.5	1.84	0.87	53
[illegible]	78	76	92.9	2.00	1.16	42

[1] Method using 3- to 2-in. coke; result reported as percentage remaining on a [illegible] screen.

[2] Method using 0.75- to 0.25-in. coke; result reported as percentage remaining on a 0.17-in. screen.

Table IV gives a condensed record of the tests made with both machine and bag shatter procedure. Conclusions to be drawn from the data are as follows:

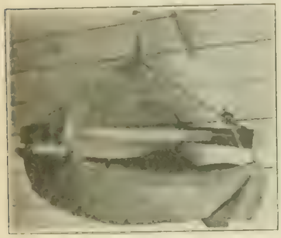

FIG. 2—BAG SHATTER TEST APPARATUS

1—Single determinations by the shatter test procedure contain an average error of 1 to 3 per cent depending on the character of the coke. Several duplicate determinations should be made.

2—Results of bag and machine shatter tests are in fair agreement.

3—A lower shatter test value is obtained when full length pieces of coke are used than when a run-of-oven sample is taken.

4—Stock coke at the Semet-Solvay plant has not deteriorated in strength as measured by the shatter test.

TABLE IV—SUMMARY OF SHATTER TEST RESULTS

Coke	Coking Time Hrs.	Size Coke Used	Type of Test	No. of Determinations	Mean Value Per cent on 2-in. Screen	Deviation from Mean Av.	Deviation from Mean Max.	Where Tested
Alabama No. 8	34	F. L.	M	5	71.8	±1.0	±2.2	Bureau of Mines Station
	34	F. L.	B	10	68.9	3.3	12.9	
	34	R. O.	M	13	76.3	3.0	12.3	
	34	R. O.	B	17	77.3	2.0	5.7	
Alabama: No. 5	16	F. L.	M	9	71.8	0.9	1.8	
	16	R. O.	M	10	69.6	2.7	6.6	
			B	8	67.1	1.7	4.6	
	15.5	R. O.	M	25	61.9	2.1	8.1	At plant
			B	23	63.3	1.5	4.8	
	15.5	R. O.	M	21	63.5	1.9	6.0	
			B	25	64.1	1.8	4.8	
	16.5	R. O.	M	26	62.5	1.3	4.0	
	16.5	R. O.	M	23	65.1	0.8	2.6	
	[illegible]	R. O.	M	24	65.0	1.1	4.0	
Alabama No. 5: Stock coke[1]	24	R. O.	M	10	67.4	1.3	2.9	
Stock coke[2]		R. O.	M	10	66.1	0.9	2.1	

F. L. indicates that pieces of coke about half the width of the oven were used for the test.

R. O. indicates that run-of-oven coke screened over a 2-in. screen was [illegible]

[1] In stock pile for one year.

[2] In stock pile for two years.

TABLE V—DAILY SHATTER TEST DATA AT BY-PRODUCT PLANT (ALABAMA NO. 5)

Month 1921-22	Number of Tests	Mean Monthly Shatter Test Value	Deviation of Daily Results from Mean Average	Deviation of Daily Results from Mean Maximum
October	[illegible]	63.3	±2.7	±7.3
November	23	67.6	3.0	9.6
December	27	68.3	2.4	7.7
January	20	[illegible]	2.5	6.5
February	[illegible]	66.2	3.4	9.8
March	10	[illegible]	1.4	3.0

Table V shows the difficulty of drawing conclusions from a single shatter test determination. The table gives condensed data from the daily shatter test records of a by-product plant. One shatter test is made each day at this plant under normal conditions. Daily results show a somewhat higher deviation from the mean value for the month than is shown in the experiments run by the writers on coke from a single oven. This indicates that there is probably some real difference in the quality of the coke from day to day, but the difference is evidentally too small to be detected by a single determination.

TABLE VI—MACHINE SHATTER TESTS WITH SIZED COKE

Through 3-in., on 2-in. screen

	Ala. No. 8 (Av. of 18 tests) (150 pieces in 50-lb. sample)				Ala. No. 5 (Av. of 9 tests) (170 pieces in 50-lb. sample)			
On	2-in.	1.5-in.	1-in.	0.5-in.	2-in.	1.5-in.	1-in.	0.5-in.
Screen analysis after test, cumulative per cent	75.3	91.2	95.9	98.7	74.3	90.1	95.3	98.2
Deviation of single determination from mean:								
Average	±2.1	1.1	0.8	.4	1.7	0.8	0.5	0.7
Maximum	±9.8	2.9	1.5	1.0	2.3	2.5	1.4	1.5

Through 5-in., on 3-in. screen

	Ala. No. 8 (Av. of 9 tests) (47 pieces in 50-lb. sample)				Ala. No. 5 (Av. of 9 tests) (60 pieces in 50-lb. sample)			
On	2-in.	1.5-in.	1-in.	0.5-in.	2-in.	1.5-in.	1-in.	0.5-in.
Screen analysis after test, cumulative per cent	75.8	86.1	92.8	96.2	71.8	86.0	94.0	98.0
Deviation of single determination from mean:								
Average	±1.8	1.1	0.8	1.2	0.9	1.3	0.7	0.6
Maximum	±3.8	2.5	1.5	2.6	1.8	2.6	1.2	2.2

Table VI shows a series of tests made on coke sized to pass a 3-in. and remain on a 2-in. screen and to pass a 5-in. and remain on a 3-in. screen. These determinations were made in the hope of securing more reproducible results, on account of the increased number of pieces in the 50-lb. sample and the uniformity obtained by the closer sizing.

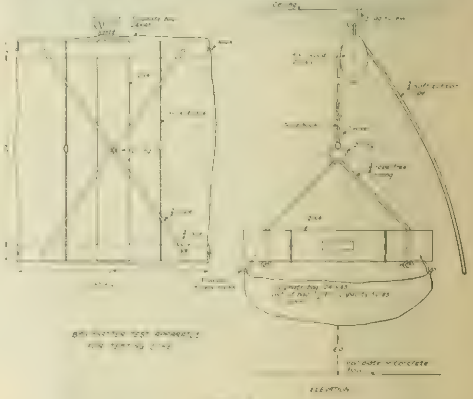

FIG. 3

Results indicate somewhat better reproducibility. The interesting development from these tests lay in the data obtained when the material passing a 2-in. screen after the shatter test was subjected to further screen analysis. It will be seen that whereas Cokes 8 and 5 show 76 per cent and 72 per cent, respectively, on the 2-in. screen, the value on the 1.5-in. screen, 86 per cent, is identical for the two cokes. When the 0.5-in. screen is used as the indicator of the shattering effect, we find that 96 per cent of Coke 8 remained on the screen as against 98 per cent of Coke 5. The producer of Coke 5, on being reproached for the inferiority of his product, might well point out that screening on a 2-in. screen is a more or less empirical procedure and that his coke showed less material passing the 0.5-in. screen than did Coke 8. It is therefore believed desirable to use a number of screens as indicators of the resistance to shattering.

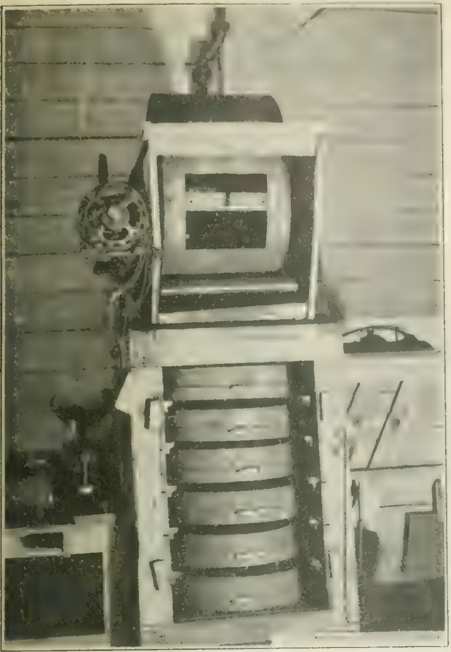

FIG. 4—TUMBLER TEST APPARATUS

Table VII compares shatter test results on four cokes where the material after the test has been subjected to screen analysis. This table indicates the desirability of using the four screens, for it shows that Cokes 8 and 5 differ little in resistance to shattering, while the Benham and Illinois cokes are more fragile, whatever screen is employed as indicator.

TABLE VII—COMPARISON OF SHATTER TEST RESULTS WHEN FOUR SCREENS ARE EMPLOYED

	Screen Analysis after Test, Cumulative Per cent			
COKE	On 2 in.	1.5 in.	1 in.	0.5 in.
Alabama No. 8	75.8	86.1	92.8	96.2
Alabama No. 5	**71.8**	**86.0**	**94.0**	**98.0**
Benham	59.0	72.5	83.7	94.9
Illinois	41.6	62.0	81.2	96.0

It is not believed advisable to change the design of the present apparatus, although more reproducible results would no doubt be obtained if a larger apparatus and correspondingly larger sample of coke were employed. From two to five duplicate determinations (the number depending on the variation between duplicate test results with the coke in question) should be made.

We desire a value from the shatter test procedure which will show the intrinsic merit of the coke, a value by which cokes varying widely in physical characteristics may be compared. From our data it is evident that attention should be paid to the size of coke pieces taken. For example, the shatter test value on Coke 8 was 72 per cent when pieces half the width of the oven were used and 76 per cent when run-of-oven coke was used. If the run-of-oven coke had been handled more before the test, this result might have been still higher.

The size and number of the large or "full length" pieces vary considerably between different plants. The advisability of employing a standard size should be considered. For the present, lacking the large amount of data necessary to determine the effect of sizing on the absolute and relative value of the shatter test result, it is recommended that large pieces about half the width of the oven be employed. With beehive coke, pieces 7 to 10 in. in length should be used, the sample being obtained as recommended in the tentative specifications of Committee D-6.

In screening the coke after the shatter test, it has been found best to put through the screen all pieces which will go through in any position. This procedure has given a better reproducible value than any method of shaking.

DETAILED DATA OF TUMBLER TEST DETERMINATIONS

The large samples of coke used for shatter test determinations were employed in making the tumbler tests. In the tentative specifications of the A. S. T. M., coke for the test is sized to pass a 3-in. and remain on a 2-in. square mesh screen. Owing to the difficulty experienced with Coke 8 in duplicating results when this size coke was employed,

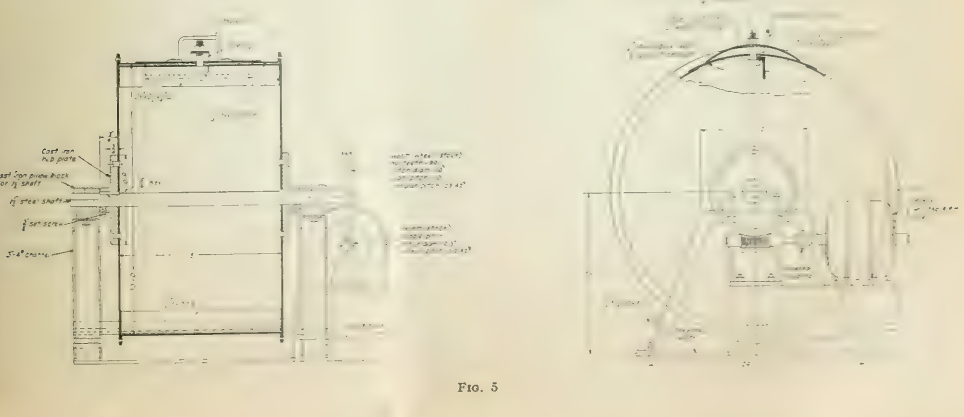

FIG. 5

a series of tests was made with various sizes of coke. A number of experiments were made to investigate the possibility of decreasing the time required for the test.

Groups of five to fifteen samples were prepared at the same time. Large pieces were broken to pass the 3-in. screen and remain on the screen chosen for the lower limit. The sample was well mixed and 25-lb. portions were weighed out for the tests.

TABLE VIII—SUMMARY OF TUMBLER TEST DATA

COKE	No. of Determinations	Screen Analysis after Test, Accumulative Per cent on Screen					Av. Diameter of Coke Pieces after Test In.	REMARKS
		2-in.	1.5-in.	1-in.	0.5-in.	0.25-in.		
Alabama:								
No. 1	2	12.7	42.0	57.4	69.9	70.1	1.15	
No. 2	2	10.0	40.0	56.5	71.0	73.0	1.14	
No. 3	2	15.1	36.1	51.2	65.6	68.1	1.10	
No. 4	2	12.8	38.0	54.2	66.1	67.0	1.10	
No. 5a	5	12.2	38.6	58.8	72.5	74.7	1.15	16.5-hr. coke
No. 5b	10	12.3	34.9	53.1	68.7	72.5	1.10	16-hr. coke
No. 5c	8	10.6	36.8	55.2	68.6	70.7	1.09	15.5-hr. coke
No. 5d	[illegible]	18.1	34.4	58.6	65.7	67.6	1.14	24-hr. coke, in stock 1 year
No. 5e	[illegible]	21.5	43.3	57.7	69.5	71.1	1.24	25-hr. coke
No. 6	3	10.2	37.0	53.7	71.2	73.6	1.10	
No. 7	3	[illegible]	45.1	59.4	70.0	71.4	1.21	
No. 8	2	10.2	43.2	59.1	72.2	73.6	1.24	
No. 9	3	11.3	38.8	57.3	71.3	73.6	1.17	
No. 10	4	14.9	38.9	54.0	66.8	67.9	1.12	
No. 11	2	18.2	41.9	61.4	65.6	73.0	1.25	
Benham	5	11.0	25.4	41.8	69.2	72.8	0.99	
Connellsville	3	18.1	39.2	52.8	68.5	70.6	1.16	
Illinois	8	2.6	12.3	33.6	72.5	77.5	0.85	
Pitch coke	3	37.6	71.1	75.1	75.3	75.6	1.16	

TABLE IX—REPRODUCIBILITY OF TUMBLER TEST DETERMINATIONS

COKE	No. of Determinations	Mean "Hardness" No.[1]	Deviation of Single Determinations from Mean	
			Average	Maximum
Alabama No. 8	13	73.5	±1.2	±2.5
Alabama No. 5	18	70.7	0.4	0.9
Benham	5	72.8	0.9	2.3
Illinois	8	77.5	0.6	2.0

[1] Percentage of original sample remaining on 0.25-in. screen after test.

TABLE X—TUMBLER TESTS WITH VARIOUS SIZES OF COKE

SIZE OF COKE		No. of Tests		"HARDNESS" NUMBER[1]					
				Alabama No. 8			Alabama No. 5		
Through	On	Ala. No. 8	Ala. No. 5	Mean Value	Deviation of Single Determinations from Mean Av.	Max.	Mean Value	Deviation of Single Determinations from Mean Av.	Max.
3-in.	2-in.	25	[illegible]	73.2	±2.3	±7.7	73.4	±0.6	±1.5
3	1	[illegible]	5	[illegible]	1.1	3.4	72.5	0.4	0.6
[illegible]	1.5	[illegible]	7	[illegible]	0.9	1.6	73.6	1.5	3.3
[illegible]	2	[illegible]	10	[illegible]	1.2	2.5	70.7	0.3	0.9
[illegible]	[illegible]	6		[illegible]	3.0	7.5	...	...	...
[illegible]	[illegible]	[illegible]		[illegible]	0.9	1.5			
[illegible]	1						77.2	0.5	1.5
[illegible]	[illegible]	[illegible]	11	[illegible]	1.2	2.9	77.0	0.8	1.4
[illegible]	[illegible]	[illegible]		81.6	1.2	2.6			
0.75	0.25			[illegible]	[illegible]	1.2	[illegible]	0.3	0.9

[1] Percentage of original sample remaining on 0.25-in. screen after test.
[2] Percentage of original sample remaining on 0.17-in. screen after test.

TABLE XI—EFFECT OF DURATION OF TUMBLER TEST AS SHOWN BY SCREEN ANALYSIS, PER CENT

Time Rotated—Minutes	15	30	45	60	75	90	105	120
[illegible]								
Alabama No. 8	46.1	33.8	24.6	17.8	13.9	12.2	9.9	8.6
Alabama No. 5	34.8	21.1	11.8	7.5	4.5	2.8	2.8	1.1
[illegible]	8.8	3.9	1.7	0.9	0.7	0.7	0.6	0.6
[illegible]								
Alabama No. 8	66.7	55.2	46.1	39.2	34.5	31.3	27.8	24.7
[illegible]	62.7	48.8	39.4	32.9	26.4	22.2	18.6	15.1
[illegible]	28.6	19.0	12.6	7.9	5.6	4.1	2.8	2.7
[illegible]								
Alabama No. 8	78.4	68.4	60.5	54.1	49.8	45.5	41.8	38.0
[illegible]	[illegible]	66.6	57.8	51.1	45.5	40.6	36.4	32.8
[illegible]	[illegible]	42.9	33.9	27.6	23.2	19.4	15.8	13.2
[illegible]								
[illegible]	[illegible]	[illegible]	[illegible]	68.4	64.2	60.4	56.2	52.9
[illegible]	[illegible]	[illegible]	[illegible]	65.2	60.3	55.9	52.5	49.2
[illegible]	[illegible]	[illegible]	[illegible]	66.7	62.1	57.9	54.4	51.9
On [illegible]								
[illegible]	[illegible]	82.3	[illegible]	70.1	66.0	62.1	57.8	54.5
[illegible]	[illegible]	[illegible]	72.9	[illegible]	62.1	57.7	54.4	51.0
Illinois	88.3	81.8	76.8	71.7	67.1	63.3	60.3	56.8
Average size of material after test, inches								
Alabama No. 8	1.75	1.51	1.32	1.17	1.06	0.99	0.91	0.84
Alabama No. 5	[illegible]	1.37	1.15	1.02	0.90	0.81	0.76	0.69
Illinois	1.14	0.96	0.85	0.74	0.68	0.63	0.58	0.56

Table VIII summarizes results obtained with the standard procedure, using 3- to 2-in. coke. Figures in the column headed "0.25-in." give the "hardness number" as usually reported. Table IX shows the reproducibility obtainable with duplicate determinations. Table X summarizes results obtained when various sizes of coke were employed. Table XI shows the effect of the duration of the test. The rotation of the drum was stopped at intervals of 15 min. over a period of 120 min. and the usual screen analysis made. The entire sample was put back in the apparatus after each screening.

The tumbler test procedure seems capable of producing more duplicable results than does the shatter test procedure, the result probably of smaller and closer sizing of the sample and the duplicable mechanical nature of the test.

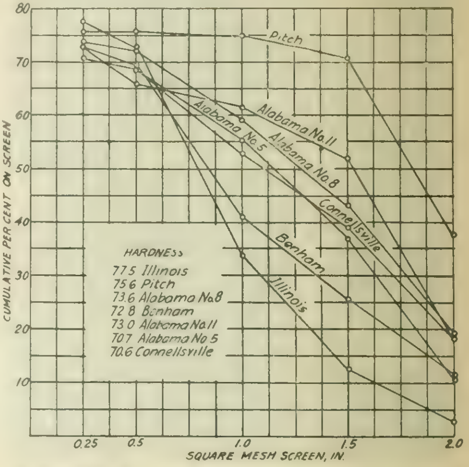

FIG. 6—SCREEN ANALYSIS OF COKES AFTER TUMBLER BARREL TEST

As seen from Table XI reducing the upper size limit (1) gives somewhat more reproducible results with Coke 8 but does not increase the reproducibility with Coke 5; (2) gives results for the two cokes which show a decreasing difference until the 0.75- to 0.25-in. size is reached, where results for both cokes are practically identical; and (3) gives results whose values are increasingly higher as the size of the material tested is diminished.

The data in Table XI suggest that two factors determine the amount of coke broken to pass the 0.25-in. screen: (1) impact, and (2) abrasion. The smaller the size of the coke pieces, the less will be the effect of impact and consequently the higher will be the "hardness" number or the percentage of coke remaining on a 0.25-in. screen after the test. This suggests further that a coke which shatters easily and is broken into small pieces early in the test period may come through the test with a very high percentage remaining on the 0.25-in. screen. The crushing due to impact of the large pieces will have been eliminated early in the procedure without necessarily crushing a large amount of the coke sufficiently fine to pass a 0.25-in. screen. This suggests, further, that the tumbler test, as at present made, has little value as a criterion for judging a variety of cokes.

Table VIII and Fig. 6 bring out this point very clearly. If judged according to the standard procedure for the tumbler test, we should say that the Illinois coke was extremely hard since it shows 77.5 per cent remaining on the 0.25-in. screen. However, we note that only 15 per cent of the Illinois coke was larger than 1.5 in. after the test, as against 36 to 60 per cent of the other cokes. As shown by the interval tests in Table XI, the Illinois coke broke up much more rapidly during the first 15 min. The "average size" figures in Tables VIII and XI were calculated for the purpose of indicating by a single value the result of the screen analysis.[11]

Comparison with the shatter test data makes it appear doubtful whether the screen analyses of the tumbler test material show any property of the coke not indicated by the shatter test. Certainly the test as at present made and reported as the percentage remaining on the 0.25-in. screen has little meaning when applied to cokes of varied physical properties.

If the abrasive factor alone is to be considered, it would seem best to use small-sized coke, *e. g.*, 0.75- to 0.25-in., and to eliminate the baffles in the apparatus. The variation in this value between the cokes tested is not large, as seen in Table III, and it is doubtful whether it has a meaning in terms of blast furnace or other operation.

ACKNOWLEDGMENT

This investigation was conducted under the direction of A. C. Fieldner, Supervising Fuels Chemist, U. S. Bureau of Mines, Pittsburgh Experiment Station, in coöperation with Committee D-6 on Coke of the American Society for Testing Materials.

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[11] Specimen calculation of average size.

BENHAM COKE

Per cent on Screen			Av Diameter In.		
2-in.	11.0	×	2.5	=	0.28
1.5-in.	14.4	×	1.75	=	0.25
1-in.	16.4	×	1.25	=	0.21
0.5-in.	27.4	×	0.75	=	0.21
0.25-in.	3.6	×	0.38	=	0.01
0.25-in.	27.2	×	0.13	=	0.03
			AVERAGE DIAMETER		0.99 in.

Sugar Formation in a Sulfite Digester[1,2,3]

By E. C. Sherrard[4] and C. F. Suhm

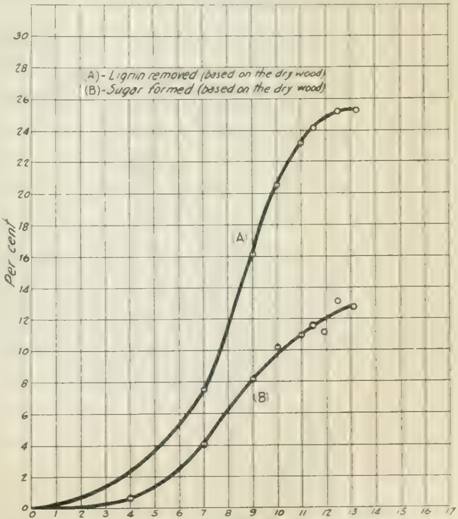
FOREST PRODUCTS LABORATORY, DEPARTMENT OF AGRICULTURE, MADISON, WISCONSIN

The results of the following investigation indicate that the rate of sugar formation is influenced chiefly by the temperature and concentration of free sulfur dioxide. Time is also a factor since prolonged cooking increases the sugar production but at the expense of the cellulose.

IN A PREVIOUS paper[5] on the manufacture of ethyl alcohol from waste sulfite liquor the desirability of investigating the rate of sugar formation in the digester was pointed out. It is known that in commercial practice a marked fluctuation occurs in the sugar content of waste sulfite liquor, a condition that is highly detrimental to the alcohol process. This variation seems to be influenced by concentration of raw acid, the sugar content of the liquor varying between 1.94 and 2.80 per cent in winter, and between 1.65 and 2.20 per cent in summer. For the ethyl alcohol process to be commercially profitable it is necessary at all times to obtain the maximum quantity of sugar with a minimum loss of pulp. This investigation was undertaken with the idea of determining the rate of formation of sugar during the pulping process and of determining the effect of sugar formation upon the quality of the pulp. An excellent opportunity was afforded for such a study since the Section of Pulp and Paper of the Forest Products Laboratory was engaged in investigating the quality of pulp produced from white spruce by the Mitscherlich process. All data contained in this paper relating to the pulp itself are taken from a paper by Miller and Swansen, which was presented before the Technical Association of Pulp and Paper Manufacturers in New York City on April 10, 1922.

One of the difficulties that such a study has always encountered has been the lack of accurate information concerning the volume of liquor contained in the digester, owing to the use of direct steam which causes a dilution to occur during the digestion. It has also been difficult to obtain accurate samples from the blow pit because of dilution by the wash water. In this case accurate data were obtained in each cook as to the dry weight of the wood used and the quantity of liquor in the digester at the time of sampling. All of these cooks were carried out on white spruce wood in an experimental digester having a capacity of 50 lbs. of pulp.

Sugar determinations were made by means of Fehling's solution, with subsequent electrolytic deposition of the copper at intervals of 1 or 2 hrs., during the progress of 8 cooks in which the conditions such as the concentration of sulfur diox-



Comparison of rate of Lignin removal with rate of Sugar formation

FIG. 1

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[1] Presented before the Section of Cellulose Chemistry at the 63rd Meeting of the American Chemical Society, Birmingham, Ala., April 3 to 7, 1922.

[2] From a thesis to be submitted in partial fulfillment of the requirements for the degree of Master of Science, University of Wisconsin.

[3] Published with permission of the Department of Agriculture.

[4] Chemist, Forest Products Laboratory, Madison, Wis.

[5] Sherrard and Blanco, *Paper*, **24**, No. 17 (1919), 746.

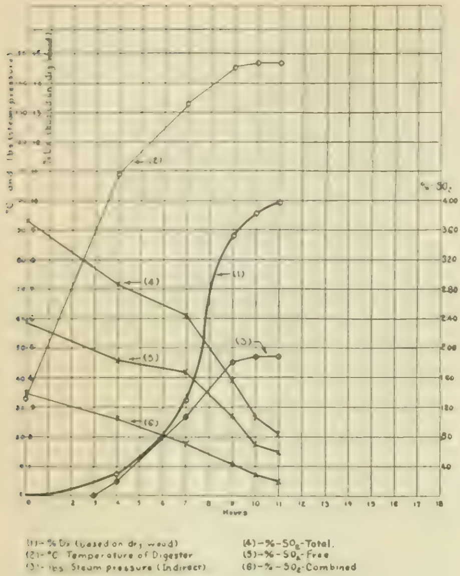

FIG. 2

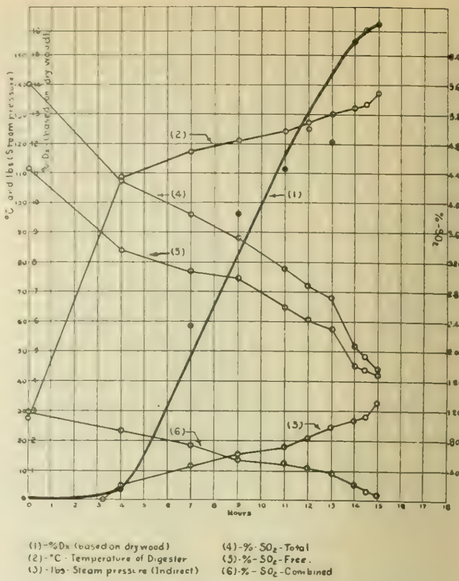

FIG. 3

ide—total, free, and combined—temperature, and pressure were held as nearly constant as possible. These cooks were blown after different periods of time in order to study the progress of the reaction in respect to the quality of the pulp and the quantity of total reducing sugar. The average per cent of total reducing sugar for all cooks at a given hour is plotted against time in Fig. 1. The total sugar is designated as glucose (D*x*), since it was determined in terms of glucose by means of Fehling's solution.

The first sugar determination at the 4th hr. indicated that but little sugar forms before a temperature of 100° C. is reached. From this point the rate of sugar formation increased with the steam pressure to about the 7th hr. at which time the rate of sugar formation rose more rapidly. The cook blown at the 7th hr. contained chips somewhat lighter in color than before cooking, but the wood had not at this point lost its original form. From the 7th to the 9th hrs. the rate of sugar production was even greater and it was during this period that the chips began to disintegrate. The partly pulped material was not screenable at the 9th hr. and required beating before it could be run into a sheet. In most cases the sugar continued to increase at about the same rate until the 10th hr., after which the reaction slowed down appreciably, although the trend was still sharply upward. The best quality pulp was obtained at the 11th hr., at which time the average quantity of sugar produced corresponded to 11 per cent of the dry weight of the original wood. Those cooks that were carried beyond the 11th hr. produced pulps that were of inferior quality both in color and strength. Apparently considerable hydrolysis of the cellulose occurred after the 12th hr. since a cook of 13$^1/_4$ hrs. gave the lowest yield of screened pulp of any of this series. During the 12th and 13th hrs. the rate of sugar production was much less, although at no time did the per cent of sugar become constant.

It is of interest to note the rate at which lignin was removed compared with the rate of sugar formation. As will be noticed from Fig. 1, these curves almost parallel each other until about the 8th hr., at which time the removal of the lignin became much more rapid. When the maximum quantity of lignin (about 90 per cent of the total) had been removed, the quantity of sugar formed corresponded to about 12 per cent of the dry weight of the wood.

Fig. 2 contains typical curves indicating variations in temperature, steam, and gage pressure, sulfur dioxide as total, free and combined, and per cent of sugar (D*x*) based on the dry weight of the wood.

The above cooks were carried out using a concentration of sulfur dioxide that averaged 3.80 per cent total, of which 2.39 per cent was free and 1.41 combined. A single cook was also carried out in which the total sulfur dioxide content was 5.60 per cent, composed of 4.46 per cent free and 1.14 per cent combined. The variables in this cook, such as pressure, temperature, etc., are shown in Fig. 3. Here again it was noted that but little sugar was formed before a temperature of 108° C. was reached. With the increased quantity of sulfur dioxide the rate of sugar formation was much more rapid after the 4th hr. than in the previous series and the final yield of total reducing sugar was 16 per cent of the dry weight of the original wood. This increase of about 3 per cent sugar was offset by about a 2 per cent loss in the cellulose yield. The quality of pulp produced in this cook was the best obtained in any of the experiments and compared favorably with the best commercial product. It is our intention to continue the investigation of the effect of increased quantities of sulfur dioxide on the sugar formation in both the Mitscherlich and Ritter-Kellner processes.

An "Association of Manufacturers of Non-Corrodible and Anti-Corrosive Products" is being organized in England by firms making stainless steel, anti-corrosive paints, boiler preservatives, and the like. It is proposed that the association shall act as an institution of anti-corrosion engineers and also as a chamber of commerce for firms making any material or appliance connected with the prevention of corrosion. A public exhibition of noncorrodible and anti-corrosive products is planned for the near future.

The Chemistry of Wood[1,2]

IV—The Analysis of the Wood of *Eucalyptus globulus* and *Pinus monticola*

By S. A. Mahood and D. E. Cable

FOREST PRODUCTS LABORATORY, DEPARTMENT OF AGRICULTURE, MADISON, WISCONSIN

IN THIS article, which is the fourth of a series by the Forest Products Laboratory on the chemistry of wood, the analysis of two new species is reported. The method of analysis employed in the earlier work has been followed closely, except for a modification of the method of preparing a sample for analysis and the inclusion in the analysis of methods for determining lignin and alpha-, beta-, and gamma-cellulose, which progress in the subject seems to justify.

Recent investigations in wood chemistry have been made by Johnson and Hovey[3] and Dore[4] in this country and Schwalbe and Becker[5] and König and Becker[6] in Europe. A proximate summative analysis of some California woods has been made by Dore. The values obtained, however, are not strictly comparable with ours, on account of differences in the methods employed.

It is desirable to determine as many well-defined splitting products of wood as possible, but until further progress is made in that direction the summation of the values obtained in an analysis appears to be of secondary importance. To merge the well-defined methoxy and acetyl groups into the ill-defined "proximate constituents," lignin and cellulose, would seem to reverse the order of progress, unless these "proximate constituents" are further analyzed, as in the more recent work of Dore.[7]

SAMPLING

The difficulties encountered in obtaining wood in a form suitable for analysis have been pointed out in a previous paper.[8] It is believed that the 80- to 100-mesh ground sawdust, the preparation of which is described there, fulfils the requirements: (1) of being a sufficiently representative sample, and (2) of affording material which will be uniformly attacked by reagents and which can be manipulated with facility in the course of the analysis.

To overcome possible objections to Schorger's procedure in using one sample for the cellulose determinations and another sample for obtaining the remaining values in the analysis, material in the same form, namely, 80- to 100- mesh ground sawdust, has been employed for all determinations.

For the purpose of determining the variations in results that might be occasioned by this change in the material analyzed, comparable runs were made on samples of *Eucalyptus globulus* in each form. The results, exclusive of the cellulose determinations which are fully considered in the paper already referred to, are given in Table I.

It will be noted that the significant differences between the results in the two series are found in those determinations where surface contact and hence the size of particle comes into play, *i. e.*, the solubility determinations, while the determinations involving partial or complete decomposition of the wood give concordant results. The variations in the values for pentosan and methyl pentosan are probably due to variations in the extraction of the latter.

The somewhat greater solubility in hot and cold water of the material which seemed in the main the coarser of the two led us to sift the 40-mesh sawdust and determine the solubility of the different fractions. The results are given in Table II.

TABLE II—EFFECT OF SIZE ON COLD WATER-SOLUBLE DETERMINATION

Fraction Mesh	Weight of Sample Grams	Soluble in Cold Water Per cent	Weight × Per cent Water-Soluble Content
40–60	16.40	5.47	89.9
60–80	14.60	5.78	84.5
80–100	2.55	5.97	15.2
100–120	3.55	5.83	20.7
120	6.59	8.05	53.1
TOTAL	43.69		263.4

$$\text{Weighted average solubility} = \frac{263.4}{43.69} = 6.03 \text{ per cent}$$

The increase in solubility shown may be due: (1) to decrease in size of particle, or (2) to concentration of the more soluble portions of the wood in the finer material, or both. Since the analytical data, excluding the solubility values, in Table I show the two samples to be uniform in composition, it is assumed that the increase in solubility shown in Table II is due largely to the effect of the size of particle.

TABLE I—EFFECT OF SIZE OF WOOD PARTICLE ON RESULTS OF ANALYSIS

(Values given are in per cent of the oven-dry (105° C.) weight of the wood)

MATERIAL	Determination Number	Ash	Solubility in Cold Water	Solubility in Hot Water	Solubility in Sodium Hydroxide 1 Per cent	Solubility in Ether	Acetic Acid by Hydrolysis	Methoxy Groups (CH_3O)	Pentosan	Methyl Pentosan
Ground sawdust passing an 80- but retained on a 100-mesh wire	1	0.26	5.30	8.36	17.91	0.62	1.56	..	17.80	2.89
	2	0.27	5.33	8.16	17.90	0.58	1.48	6.87	18.00	2.59
	Mean	0.27	5.32	8.26	17.90	0.60	1.52	6.87	17.90	2.74
Sawdust passing a 40-mesh sieve	1	0.21	6.47	9.78	18.09	0.79	1.56	6.64	17.27	3.06
	2	0.19	6.52	9.69	18.10	0.77	1.34	7.07	17.52	3.00
	Mean	0.20	6.50	9.74	18.10	0.78	1.45	6.83	17.39	3.03

The data show that either form of material will give results that are essentially comparable, but since the 80- to 100-mesh material has been shown to be most suitable for the cellulose determination, this material has been used through the present investigation.

LIGNIN

When the cellulose in wood is removed by hydrolyzing it to soluble forms, a residue is left which is fairly constant, even through the hydrolytic agent and the conditions of hydrolysis are varied somewhat.[6] The residue retains a surprising similarity to the lignin of the original wood, considering the rather drastic treatment necessary for the

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[1] Presented before the Section of Cellulose Chemistry at the 63rd Meeting of the American Chemical Society, Birmingham, Ala., April 3 to 7, 1922. Published with permission of the Department of Agriculture.

[2] The earlier papers of this series were published in THIS JOURNAL, **9** (1917), 556, 624, 748, by Dr. A. W. Schorger, whose work the present authors have continued.

[3] *Paper*, **21**, No. 23 (1917), 36.

[4] THIS JOURNAL, **11** (1919), 556; **12** (1920), 264.

[5] *Z. angew Chem.*, **32** (1919), 229.

[6] *Ibid.*, **32** (1919), 155.

[7] THIS JOURNAL, **12** (1920), 472, 476.

[8] *Ibid.*, **12** (1920), 873.

hydrolysis of the cellulose. For example, the residue obtained by treating the wood of *E. globulus* with 72 per cent sulfuric acid gave the characteristic color for lignin when treated with chlorine and sodium sulfite. The changes which occur are apparently superficial and may involve the loss to a greater or less extent of methoxy and acetyl groups and furfural-yielding constituents. The values obtained, however, appear to be sufficiently constant to warrant their determination in an analysis of wood.

Preliminary experiments showed 72 per cent sulfuric acid, employed by Ost and Wilkening[9] in the hydrolysis of cellulose, to be a more efficient hydrolytic agent and more convenient to handle than hydrochloric acid. There is considerable difficulty in filtering the lignin residues, owing to the more or less colloidal nature of the solution. This can be largely overcome by boiling the solution after dilution.

In order to adopt a method of procedure, it was necessary to determine (1) the time of exposure to the acid necessary to effect complete hydrolysis, and (2) the effect of boiling the solution. By varying the time of exposure to sulfuric acid it was found that a period of 16 to 24 hrs. is sufficient for complete hydrolysis. The values obtained for western white pine, *Pinus monticola*, calculated on the basis of the oven-dry wood, follow:

TABLE III—EFFECT OF TIME OF EXPOSURE ON LIGNIN DETERMINATION

Time of Exposure Hours	Lignin Content Per cent
4	27.77
8	27.32
16	27.09
24	27.03

The effect of boiling is to reduce slightly the yield of non-cellulose material, as shown by the following results, also on western white pine.

TABLE IV—EFFECT OF TIME OF BOILING ON LIGNIN DETERMINATION

Time of Boiling Minutes	Lignin Content Per cent
Not boiled	28.89
15	27.07
45	26.82
120	26.76

It will be noted that a 15-min. boiling reduces the yield approximately 2 per cent, and that practically no further loss takes place on continued boiling.

In view of the above results, the following procedure was adopted for the determination of the lignin values reported in this paper. It is possible that the conditions are not the optimum for hardwoods.

Two grams of air-dried material are extracted for 4 hrs. with a minimum boiling-point mixture of alcohol and benzene. After removal of the solvent by suction the sample is treated with ten times its weight of 72 per cent sulfuric acid. The sample and acid are intimately mixed with a stirring rod, causing the wood to become completely disintegrated after a few hours. After hydrolysis has been allowed to proceed at room temperature for 16 hrs., the acid is diluted to a concentration of 3 per cent. The solution is then boiled under an air-cooled reflux condenser for 2 hrs. The lignin is then filtered on a tared alundum crucible (previously treated with acid), washed free from acid with hot water, dried at 105° C., and weighed.

CELLULOSE

The cellulose values obtained in the analysis of wood are quite constant for conifers on the one hand and broad-leafed trees on the other. The celluloses from these two groups are differentiated by the amounts of pentosan they contain.[1] Future work will probably show other differences, not only between the celluloses from these two groups but also between that from individual species of each group. It seemed desirable, therefore, to introduce into the analysis the mercerization test[10] as a possible means of further differentiating the celluloses isolated by chlorination.

RESULTS

The results of the analysis of four representative samples each of western white pine and eucalyptus are given in Table V. The pine was grown in Bonner County, Idaho, and the eucalyptus in Santa Clara County, California.

DISCUSSION OF RESULTS

In most cases the results parallel rather closely those obtained by Schorger for conifers and broad-leafed trees, respectively. Western white pine is shown to be very similar in composition to longleaf pine, the most notable difference between the two being in their relative solubility in hot and cold water and alkali, longleaf pine being quite appreciably more soluble in all three reagents.

Eucalyptus does not approach the hardwoods already analyzed in this series as closely in composition as western white pine does the conifers. Among the most notable differences is the low-ash content of eucalyptus, which corresponds more nearly with that of the conifers. The yield of acetic acid by hydrolysis from eucalyptus wood is much less than that from the hardwoods previously analyzed. It has been shown, however, that eucalyptus yields nearly as much acetic acid by destructive distillation as the hardwoods ordinarily distilled.[11]

The cellulose isolated from the two woods contains approximately the same amount of alpha-cellulose. It is interesting to note that the remaining portion of the cellulose in the case of eucalyptus is almost entirely gamma-cellulose, while in the pine it is about equally divided between beta- and gamma-cellulose. These resolution products of the celluloses should be studied further.

The lignin values are higher for pine than for eucalyptus. In other words, the conifer appears to be the more highly lignified, a fact contrary to the usual botanical conception of the relative lignification of these two groups of plants. It should be noted that the cellulose and lignin values for the individual samples compensate, higher lignin values being obtained from samples with a lower cellulose content.

TABLE V—COMPLETE ANALYTICAL RESULTS ON WHITE PINE AND EUCALYPTUS
(Results in percentage of oven-dry (105° C.) sample)

[illegible]	Sample No.	Moisture in Air Dry Sample	Ash	SOLUBILITY IN Cold Water	Hot Water	Ether	1 Per cent NaOH	Acetic Acid by Hydrolysis	Methoxy Groups (CH_3O)	Pentosan	Methyl Pentosan	Cellulose	IN CELLULOSE Alpha	Beta	Gamma	Pentosan	Methyl Pentosan	Lignin
[illegible]	1	6.18	0.21	2.60	3.35	4.00	13.97	1.21	4.38	6.75	3.41	58.53	70.58	18.16	11.26	4.47	1.59	27.22
	2	7.68	0.20	1.73	2.57	4.42	12.70	0.94	4.59	7.19	3.25	62.29	64.34	10.69	24.97	5.66	2.97	24.15
	3	[illegible]	[illegible]	[illegible]	7.25	3.98	15.92	1.37	4.86	6.48	3.33	59.40	74.29	9.17	16.54	5.19	1.68	27.55
	4	7.15	0.19	4.40	4.78	4.63	16.51	1.09	4.41	7.46	2.90	58.61	49.27	27.27	23.46	5.96	1.56	26.82
	Mean	7.00	0.20	3.16	4.49	4.26	14.78	1.03	4.56	6.97	3.22	59.71	64.61	16.32	19.06	5.33	1.95	26.44
Eucalyptus [illegible]	1	6.99	0.23	2.65	4.41	0.54	16.57	2.31	7.11	21.41	1.97	59.67	67.85	2.11	31.04	20.35	3.92	24.04
	2	6.55	0.20	4.93	6.96	0.52	18.42	1.97	6.37	20.66	2.14	58.53	69.75	0.00	31.25	21.62	2.44	25.24
	3	6.87	0.27	5.31	8.26	0.60	17.90	1.51	6.87	17.90	2.74	56.45	68.99	0.00	31.01	20.10	2.24	25.07
	4	5.90	0.24	5.79	8.27	0.59	21.40	1.62	6.56	20.39	2.48	55.83	...	...	...	21.76	1.26	26.74
	Mean	6.58	0.24	4.67	6.98	0.56	18.57	1.85	6.73	20.09	2.33	57.62	68.86	0.70	31.10	20.96	2.46	25.27

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[9] C. F. Cross and E. J. Bevan, "Researches on Cellulose," 3 (1905–10), 23.

[10] Cross and Bevan, "Researches on Cellulose," 3 (1905–10), 23; Cross and Bevan, "Paper-Making," 1916, 97; Schwalbe, "Chemie der Cellulose," 1911, 637.

[11] *U. S. Dept. Agr., Bull.* 508.

The Calorific Value of American Woods[1]

By S. W. Parr and C. N. Davidson

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WOOD as a fuel may have war-time interest only, or it may be a matter of regional concern or of significance in special industries where wood waste accumulates to a point where it must be disposed of. These conditions may in themselves be a sufficient reason for desiring to know the calorific value of such material. There are other reasons also worth mentioning. At the time this work was carried out (1916), at least, there were no values given in the literature for American woods. Similarly, it is not far wrong to state that there were no values that were worth anything given in the literature for any woods in any country. For example, Count Rumford's values are frequently given in works of reference.[2] His work was done 110 years ago,[3] and while he had the correct idea as to the proper method of procedure, his results were little better than approximations. His sample was burned in a current of air and the products of combustion were conducted through a copper coil surrounded by a known volume of water. His thermometer he made himself, but the chief elements of error were doubtless the uncertainty as to the completeness of combustion and the vague ideas concerning the amount or nature of the moisture present in the wood. Again Groves and Thorp, in their work on "Chemical Technology,"[4] tabulate the heat values for wood as derived by Berthier, Winkler, and Schödler and Peterson. These values refer to partially dry, well-seasoned wood, but the real content of moisture is uncertain. Worse than this, however, is the fact that all these values were determined by calculation from the weight of a lead button reduced from litharge. The equivalent of oxygen taking part in the reaction is used as a measure of the amount of heat, according to the so-called Welter law which held that a fixed ratio existed between oxygen consumed and heat produced, no matter what combinations were involved. The results obtained do not have the value of a good guess and would need to be increased by about 50 per cent to come even approximately near the true values. Berthier's results were published in 1835. This date, together with the method employed, suggests the absurdity of repeating them except as curiosities. They do not have as much merit as Rumford's values obtained some 20 years previous, the errors being about twice as great.

In other works of reference as Poole's "Calorimetry" (1903), Brame's text on "Fuels" (1914), etc., the values quoted are those of Gottlieb.[5] These values are more recent and have the advantage that they were calculated to the oven-dry basis. He used a calorimeter with oxygen as the medium of combustion, but it was of the constant pressure type, which seems not to have been capable of as great refinement in results as should characterize the values which are to be used continuously as a standard of reference. Results obtained 40 years ago with an apparatus which to-day is not recognized as standard should at least be worked over for correction or verification. In Poole's tables, note should be made of two results by Mahler, which doubtless are reliable. They are given as "cinder and water deducted," while the seven values of Gottlieb are not indicated in Poole as to their basis of reference. The original article, however, shows that they refer to dry or "moisture-free" material. The moisture factor was determined by drying for 12 to 15 hrs. in a hot air bath maintained at 115°.

It is evident from this brief survey that the determination of the free moisture present is in as much need of review as the calorific value. Indeed, the latter factor is of little worth without the former. Even greater ambiguity is found in the use of terms than is found in the case of coal. Dry wood is understood to mean well-seasoned wood, and there seems to be a reluctance to recognize a sharp line of demarcation between the free moisture and the very large amount of hydrogen and oxygen chemically combined in the H_2O ratio $(C_6H_{10}O_5)_x$ of cellulose.

Our experiments were first directed toward the determination of the "end-point," if there was one, for the free moisture. Was it obscured by uncertain volatilization of sap constituents, or oxidation of unsaturated compounds in the drying process, or possibly an initial breaking down of the cellulose molecule, giving off seemingly free moisture?

Six samples of dry, well-seasoned wood were prepared in the form of fine sawdust. Approximately 1-g. samples were heated at 105° each for 1-, 2-, 3-, 4-, 5-, 6- and 7-hr. periods, using a new sample for each period and drying in an atmosphere of air and also in carbon dioxide, using a Freas oven with electric heat control. All samples were cooled 20 min. over concentrated sulfuric acid before weighing. The entire series was repeated at 137°, using an atmosphere of air and repeated with carbon dioxide. The curves show interesting results, but only one of each series is given here. It is evident from Fig. 1 that a substantial equilibrium is established after drying in air at 105° for one hour. A small increase in the air-drying loss is noted up to the end of the third hour. In the use of carbon dioxide as the atmosphere of the oven (not shown) the same percentage of loss is reached at the end of 3 hrs., after which the lines are practically straight.

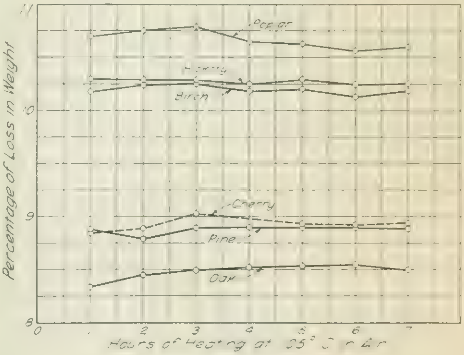

FIG. 1

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[1] Presented before the Division of Industrial and Engineering Chemistry at the 63rd Meeting of the American Chemical Society, Birmingham, Ala., April 3 to 7, 1922.

[2] Groves and Thorp, "Chemical Technology. Vol. 1—Fuel and Its Applications," **1889**, 338.

[3] *Nicholson's Journal*, **32** (1812), 105; **35** (1813), 95.

[4] "Fuel and Its Applications," **1** (1889), 360.

[5] *J. prakt. Chem.*, **28** (1883), 414.

The conclusion from these curves is that by drying at 105° for one hour in an atmosphere of air, the loss whatever it is, has reached a constant quantity.

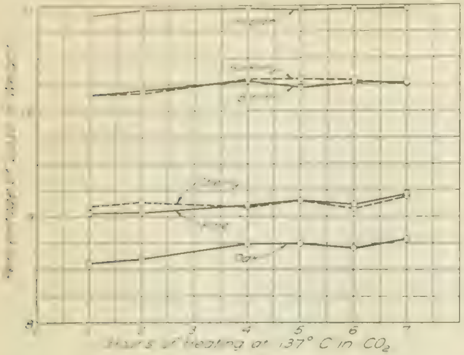
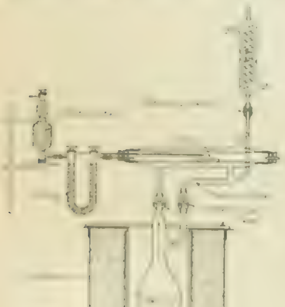


FIG. 2

One other set of curves is worth noting. In Fig. 2 the temperature used was 137° and the atmosphere was carbon dioxide in order to eliminate possible oxidation from the presence of free oxygen. Here the values are stabilized at the end of the first hour, but they are in most cases a trifle higher, usually about 0.2 to 0.3 per cent, though in the case of birch and hickory the difference is not appreciable. The conclusion from a comparison of these two charts suggests the probability of a slight loss of volatile constituents other than water at the higher temperature. This was verified by repeating the drying on a few samples, using the higher temperature with an atmosphere of air and collecting and weighing the water discharged. The apparatus used is shown in outline in Fig. 3. It is a slight modification of the apparatus described by Prof. John White.[6] The drying chamber is maintained at 135° to 140°, it being surrounded by xylene vapor. The loss in weight is consistent with the loss as shown in Fig. 2. The weight of water absorbed is uniformly less than the total decrease in weight, verifying the point already noted that some volatile constituents of the wood other than water are discharged at 135° to 140°. This material is so small at this temperature, averaging about 0.3 per cent, that it is considered negligible at a drying temperature of 105°. It is, at any rate, of the same order of difference between water and volatile constituents as the material commonly recognized as being discharged from coal under the same conditions of drying.



In determining the calorific values, the same samples were employed with the moisture content taken as shown after one hour's drying as in Fig. 1, the heat values being calculated to the dry basis. The instrument used was of the Mahler type, platinum lined and under adiabatic control by having accessible both hot and cold water for modifying the temperature of the jacketing water to conform to the inner system containing the combustion bomb. The circulation of the jacketing water is secured through the cover as well as on all sides and bottom of the inner receptacle. The results are given in Table I. Corrections were made for the nitric acid formed in the combustion, the fuse wire, etc., as prescribed by the standard method adopted by the AMERICAN CHEMICAL SOCIETY.[7]

TABLE I

WOOD	Per cent H_2O at 105° C. 1 hr.	B. t. u. (as Recd.)	B. t. u. (Dry Basis)
Pine	8.88	8040.0 8055.5 8054.0	
AVERAGE		8049.8	8836.2
Oak	8.35	7829.0 7855.5 7840.0	
AVERAGE		7841.5	8555.7
Hickory	10.30	7594.2 7561.0 7578.8	
AVERAGE		7578.0	8448.1
Cherry	8.85	7852.0 7867.7 7860.0	
AVERAGE		7859.9	8623.0
Birch	10.18	7607.2 7593.0 7592.2	
AVERAGE		7597.4	8458.4
Poplar	10.69	7709.8 7725.2 7712.5	
AVERAGE		7716.1	8639.6

A comparison with the values as given by Gottlieb for corresponding varieties of wood, so far as they were represented in our samples, will be of interest as follows:

TABLE II—B. T. U. VALUES

WOOD	GOTTLIEB	PARR AND DAVIDSON	DIFFERENCE
Oak	8316	8555.7	+239.7
Pine	9153	8836.0	−317.0
Birch	8586	8458.4	−127.6

An inspection of the table shows that the Gottlieb results have a variation from our own of ±3 per cent. Considering the fact that woods, even of the same varieties, grown in different countries indicate no greater divergence, it is fair to conclude that the values obtained by Gottlieb should be accepted as reasonably accurate. It must be concluded, however, that considering the care and type of instrument employed in this work, the values as given in Table I fairly represent the correct heat values for the several samples worked on and may be taken as representative values for American woods.

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[6] *J. Frank. Inst.*, **173** [illegible].

[7] "Report on Sampling and Analysis of Coal," THIS JOURNAL, **5** (1913), 517.

New Standard Sample of Bureau of Standards

A new standard sample of tin-base bearing metal No. 54 is now being issued with a provisional certificate. This sample has the approximate composition: Tin 88 per cent, antimony 7 per cent, and copper 4 per cent. In addition it contains small amounts of lead, iron, bismuth, and arsenic. The price of this sample is $2.00 per 140 g., prepaid or parcel post C. O. D.

Benzoic acid No. 48*a* and benzoic acid No. 39*a* have been discontinued. Benzoic acid No. 39*b* replaces both of these and is issued for use both in acidimetric and calorimetric work. The price of this sample is $2.00 per 30 g.

Studies on Rancidity[1]

I—The Influence of Air, Light, and Metals on the Development of Rancidity

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The following paper records experiments on the effect of metals on the development of rancidity in fats and oils.

Fats, even when kept in contact with metals, exposed to light and at summer temperatures, did not become rancid provided that air was excluded. However, the development of rancidity was not prevented when fats, alone and in contact with metals, were kept in a Novy jar through which carbon dioxide, presumably air-free, was passed continuously.

Fats stored, with and without contact with metals, in an atmosphere of oxygen developed rancidity at an earlier date, and the development of rancidity progressed more rapidly, than when the same fats were held in an atmosphere of air, all other conditions being the same.

The development of rancidity was hastened when the fats or oils were in contact with metals, provided there was free access of air or oxygen. Some metals, however, acted more energetically than others. The action of the metal was independent of the corrosive action of the fat upon the metal. In other words, metals hastened the production of rancidity in fats even when the metals themselves were not attacked.

Light was necessary for the development of rancidity in fats exposed to air and not in contact with metals, but fats stored in contact with metals developed rancidity even when protected from light. In other words, light in the absence of metals appeared to exert the same effect as was exerted by metals in the absence of light.

In one test it was indicated that the direct part taken by moisture in the development of rancidity, at least in comparison with the other factors discussed, is negligible.

It may be concluded that air; oxygen, alone or in combination; light; and metals are among the factors which influence the development of rancidity in fats and oils.

DURING an investigation of the action of fats and oils upon metals[2] it was noted by one of us that rancidity developed more rapidly when these glycerides were held in metallic containers or in contact with metals than when they were held in glass vessels. Since a search of the literature did not disclose any similar observation by others, the experimental work presented in this paper was conducted.

The detection of rancidity through the sense of smell or of taste, especially in the incipient stage, is not to be relied upon, and therefore in all of the work the Kreis test, which is most sensitive to the chemical changes that finally express themselves in the form of rancidity, was applied at the time the odor was noted. In this test 2 cc. of the fat or oil under examination are dissolved in 2 cc. of a 1 per cent solution of phloroglucinol in ether, 2 cc. of commercial hydrochloric acid are added, and the whole is well shaken, the appearance of any color being noted. Rancid fats cause the development of a more or less pronounced pink shade, the degree of change in the fat being indicated by the depth of color produced. No color is given by freshly prepared fats.

Inasmuch as rancidity was recognized as being due to chemical changes in the fats, the various factors which, during the progress of the investigation, appeared to have an influence either in promoting or retarding its production, were noted, with the view of later determining the part played by each in the phenomena produced.

EFFECT OF METALS AND LIGHT IN PRODUCTION OF RANCIDITY IN FATS EXPOSED TO AIR

SERIES I—The fat used in all of the experiments was rendered in the laboratory from the leaf fat of a freshly killed hog and in each test 60 g. of fat were employed. With but two exceptions (small cups of tin and galvanized iron) the containers were glass vessels of 150-cc. capacity. The metals used were in sheet form, cut approximately of the same size, and rolled into half cylindrical shapes which, when placed on end in the fat or oil, projected slightly above the surface.

Expt. A—Three glass beakers, one containing lard and lead, one lard and copper, and the third lard alone, covered to exclude dust, were placed on a laboratory table exposed to light.

Expt. B—A beaker containing lard and lead, and one containing lard alone, also covered, were placed in a dark closet situated directly under the table mentioned in Expt. A.

Expt. C—Lard in a galvanized iron cup, lard in a tin-plated cup, and lard in a glass beaker, all containers being of the same diameter and also covered, were placed in the light on the table above referred to.

On the fifth day and at frequent intervals thereafter the odor of each sample was noted and the Kreis test was applied, with the results shown in Table I.

It will be seen that the fats in contact with metals became rancid much more rapidly than those in contact with glass alone. The rancid odor became apparent in lard and lead on the seventh day, in lard and copper on the sixth day, and in lard alone on the twenty-sixth day; a positive Kreis reaction appeared with lard and lead on the sixth day, with lard and copper before the fifth day, and with lard alone on the twenty-third day. In Tests 4 and 5 the lard and lead gave a positive Kreis reaction on the fifth day, and lard alone on the twenty-seventh day. The same relation between the rate of production of rancidity in fats kept in metallic and in glass containers, is maintained in Tests 6, 7, and 8.

In regard to the effect of light, there appeared to be no marked difference in the rate of production of rancidity in fats kept in the dark and those kept in the light; however, the evidence upon this point, in view of the limited number of tests, cannot be regarded as conclusive.

EFFECT OF LIGHT ON PRODUCTION OF RANCIDITY

SERIES IV—The results obtained in Series I were considered inconclusive, and since some observers[3] have maintained that light is necessary for the production of rancidity, tests were conducted to settle the question more definitely. The samples were placed in blackened light-tight Erlenmeyer flasks, plugged with cotton, and kept under blackened light-tight beakers. The following are the tests conducted:

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[1] Received April 27, 1922. Published with permission of the Department of Agriculture.

[2] James A. Emery, "The Use of Metallic Containers for Edible Fats and Oils," U. S. Dept. Agr., Bur. Animal Ind., 26th Annual Report, **1909**.

[3] Ritsert, *Naturw. Wochenschr.*, Berlin, **5** (1890), 331, 354, 364; Reinmann, *Centr. Bakt. Parasitenk., II Abt.*, **6** (1900), 131, 166, 209; Scala, *Chem. Zentr.*, **1896**, 520, Winckel, *Z. Nahr.-Genussm.*, **9** (1905), 90.

TABLE I—EFFECT OF METALS AND LIGHT IN PRODUCTION OF RANCIDITY IN FATS EXPOSED TO AIR

	LIGHT						DARKNESS				LIGHT					
	1		2		3		4		5		6		7		8	
Date 1912 4/10	Lard and Lead (Beaker)		Lard and Copper (Beaker)		Lard (Beaker)		Lard and Lead (Beaker)		Lard (Beaker)		Lard in Tin Cup		Lard in Galv. Iron Cup		Lard (Beaker)	
	Odor	Kreis Test	Odor	Kreis Test	Odor	Kreis Test	Odor	Kreis Test	Odor	Kreis Test	Odor	Kreis Test	Odor	Kreis Test	Odor	Kreis Test
4/15	–	–	–	+3	–	–	–	+2	–	–	–	+1	–	–	–	–
4/16	–	+2	+1	+4	–	–	+1	+3	–	–	+1	+3	...	+1	–	–
4/17	+1	+3	+2	+4	–	–	+2	+4	–	–	+1	+4	+1	+2	–	–
4/18	+2	+4	+2	+4	–	–	+2	+4	–	–	+2	+4	+1	+3	–	–
[illegible]	+2	+4	+3	+5	–	–	+2	+5	–	–	+2	+5	+2	+3	–	–
4/23	+3	+5	+3	+5	–	–	+2	+5	–	–	+3	+5	+2	+4	–	–
4/26	+3	+5	+3	+5	–	–	+3	+5	–	–	+3	+5	+3	+4	–	–
[illegible]	...	...	...	...	–	–	...	...	–	–	...	...	+3	+5	–	–
[illegible]	...	...	...	...	–	–	...	...	–	–	...	...	...	...	–	+1
[illegible]	...	...	...	...	+2	+1	...	...	–	+2	...	...	...	...	–	+2
5/24	...	...	...	...	...	+4	...	...	...	...	...	...	...	...	+2	+3

– = Negative; + = Positive; suffixed numerals used to indicate degree.

This set consisted of two clear 100-cc. flasks, one of which contained 50 cc. of lard, the other 50 cc. of lard in which a sheet of copper had been placed, and of two blackened 100-cc. flasks, one of which contained 50 cc. of lard alone, and the other 50 cc. of lard and a sheet of copper (2 in. by 2 in.).

These flasks were plugged with cotton, and placed upon the table, the blackened flasks being placed under blackened beakers. After 16 days the first observations were made.

	ODOR	KREIS TEST
CLEAR FLASK:		
Lard	Good	Very faint
Lard + Cu	Rancid	Intense
BLACKENED FLASK:		
Lard	Good	Negative
Lard + Cu	Rancid	Intense

As the lard in the blackened flask showed no evidence of rancidity, while the lard in the clear flask showed faint evidences of rancidity, the flasks were kept upon the table for 40 days longer.

	ODOR	KREIS TEST
CLEAR FLASK:		
Lard	Rancid	Intense
Lard + Cu	Very rancid	Very intense
BLACKENED FLASK:		
Lard	O. K.	Negative
Lard + Cu	Very rancid	Intense

The outstanding feature of these tests was that the lard alone in the blackened flask showed no rancidity after 56 days, while the lard in the clear flask was strongly rancid at that time, and probably faintly rancid on the sixteenth day. Further, the lard containing copper in the blackened flask was not quite as rancid after 56 days as was the lard and copper in the clear flask; the difference was so very slight, however, that it may be said that little or no difference exists in the rate of production of rancidity in fats exposed and not exposed to light, when these fats are in contact with metals. A larger number of such tests, with observations made at more frequent intervals, would afford more interesting and more conclusive results than were obtained, and would probably yield valuable information regarding the chemistry of rancidity.

RELATIVE EFFECT OF AIR, CARBON DIOXIDE, AND OXYGEN IN PROMOTING RANCIDITY

SERIES II—Ritsert,[3] who studied the effect of air, carbon dioxide, and other gases on fats held in glass containers, found that next to oxygen, carbon dioxide was the most rapidly absorbed. He noted, however, that, although the fats stored in carbon dioxide developed acidity and a flat taste, they did not become rancid.

It is generally believed that the presence of air, or the oxygen of air, is necessary for the production of rancidity. Donath,[4] whose observations have been confirmed by studies (as yet unpublished) made in this laboratory demonstrated that as a rule fatty acids act upon metals only in the presence of oxygen. The following tests were conducted concerning the rate of production of rancidity in fats stored in atmospheres of air, oxygen, and carbon dioxide:

Fifty grams of freshly rendered leaf lard were placed in each of nine 100-cc. beakers. A sheet of copper was placed in each of three of these, a sheet of tin in each of three others, while to the remaining three no metal was added. The metallic sheets were of uniform size (1.5 in. by 1.5 in.). The beakers were then divided into three groups, each of which consisted of one containing lard and copper, one containing lard and tin, and one containing lard alone. One set was placed on the laboratory table under an open bell jar, another was placed in a Novy jar, through which a stream of oxygen was allowed to flow constantly; and the remaining set was placed in a Novy jar, through which carbon dioxide, obtained by the action of sulfuric acid on marble, was continually being passed. Both the carbon dioxide and oxygen were dried by passing through calcium chloride. Results of these tests are shown in Table II.

In an atmosphere of oxygen, both in the presence of a metal and when no metal was in contact with the fat, rancidity developed at an earlier date, and progressed more rapidly, than in samples held in an atmosphere of carbon dioxide or in air. It was also noted that the fats held in carbon dioxide became rancid a trifle more slowly than did those held in air, although this difference is but slight.

Carbon dioxide had been used in this test solely for the purpose of excluding oxygen. The production of rancidity, and its rather rapid development, in the fats stored in an atmosphere of carbon dioxide was not only not anticipated, but was surprising. While it was believed that the oxygen of the air had been replaced by carbon dioxide, in the Novy jar in which the fats were held, the jar had been opened from time to time for the purpose of extracting samples of fat for examination, and an opportunity was thus afforded for the fat to absorb oxygen. To avoid this the test was repeated in the following manner:

Into each of three 50-cc. beakers, all of the same diameter, 30 cc. of freshly rendered leaf fat which had an acidity of 0.22 per cent (calculated as oleic acid) were added. In one beaker, a square of copper and in a second a square of tin was placed. A third beaker contained the lard alone. The squares of metals each measured 2 in. by 2 in. and were thoroughly cleaned and polished before being placed in the fats.

TABLE II—RELATIVE EFFECT OF AIR, CARBON DIOXIDE, AND OXYGEN IN PROMOTING RANCIDITY

	AIR						OXYGEN						CARBON DIOXIDE					
Date 1912 6/[illegible]	Lard and Tin		Lard and Copper		Lard		Lard and Tin		Lard and Copper		Lard		Lard and Tin		Lard and Copper		Lard	
	Odor	Kreis Test	Odor	Kreis Test	Odor	Kreis Test	Odor	Kreis Test	Odor	Kreis Test	Odor	Kreis Test	Odor	Kreis Test	Odor	Kreis Test	Odor	Kreis Test
6/28	[illegible]	[illegible]	–	+3	–	–	+1	+3	+1	+4	–	–	–	+2	+1	+3	–	–
7/1	+1	+2	[illegible]	[illegible]	–	–	+1	+3	+1	+5	–	–	–	+2	+1	+3	–	–
7/3	+1	+3	+1	+5	–	–	+2	+4	+2	+5	–	+1	–	+2	+2	+4	–	–
7/5	+2	+4	+2	+5	–	+1	+2	+4	+2	+5	–	+1	+1	+3	+2	+4	–	+2
7/10	+2	[illegible]	+2	+5	–	+1	+2	+5	+2	+5	–	+2	+1	+4	+2	+5	–	+2
7/12	+2	[illegible]	[illegible]	[illegible]	–	+1	+2	+5	+2	+5	+1	+2	+2	+4	+2	+5	+1	+3
7/16	+2	[illegible]	[illegible]	[illegible]	–	+2	+2	+5	+2	+5	+1	+3	+2	+5	+2	+5	+1	+3

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[4] *Dinglers polytech. J.*, **294** (1894), 186.

A second and third set of beakers, identical in all details with the above described, were prepared at the same time.

One set consisting of beakers containing lard, lard with tin, and lard with copper, was placed on the laboratory table, protected from dust but exposed to light and air.

Another set was placed in a Novy jar containing calcium chloride, and through the jar a stream of oxygen, previously dried by passage through calcium chloride, was continuously passed. It was placed on the table beside the first set.

The third set was placed in a second Novy jar, which contained calcium chloride, and through which a stream of carbon dioxide was continuously passed both day and night. The carbon dioxide was generated in a Kipp generator from marble and sulfuric acid, and was washed and dried before entering the jar. The stream of carbon dioxide was interrupted only when it was necessary to recharge the Kipp generator, and on such occasions the jar was closed to prevent access of air. This Novy jar remained unopened from October 14 to November 21. The fats in the first and second sets were tested for rancidity on October 28 and November 8. The results of the Kreis test are shown in Table II*a*.

Again those fats held in a Novy jar through which carbon dioxide was passed continuously, developed rancidity. It is true that the complete absence of air, or oxygen, was not proved, but the amount of residual, or adventitious, air or oxygen present must have been, in comparison with the amount of carbon dioxide, extremely small. These experiments certainly indicate that carbon dioxide may promote the production of rancidity. While this observation was considered important and interesting, time did not permit of a more extended investigation.

TABLE II*a*—RELATIVE EFFECT OF AIR, OXYGEN, AND CARBON DIOXIDE IN PROMOTING RANCIDITY

DATE 1912 10/14	Atmosphere of Air			Atmosphere of Oxygen			Atmosphere of CO_2		
	Lard	Lard and Tin	Lard and Copper	Lard	Lard and Tin	Lard and Copper	Lard	Lard and Tin	Lard and Copper
				Kreis Test					
10/28	–	–	+5	+3	+4	+5	Not tested	Not tested	Not tested
11/8	–	+3	+5	+5	+5	+5	Not tested	Not tested	Not tested
11/21	+2	+4	+5	+5	+5	+5	+1	+4	+5

EFFECT OF EXCLUSION OF AIR ON DEVELOPMENT OF RANCIDITY

SERIES III—Since the rate of development of rancidity in fats stored in air and carbon dioxide appeared to be practically the same, the method which had been planned of securing exclusion of air by replacing it with carbon dioxide, both with and without contact with metals, was abandoned. Complete exclusion of air was obtained by completely filling the container with the melted fat and then forcing a cork stopper into the flask. The fat which was forced out was removed by washing with ether, and the cork was then sealed with wax. The effect of the presence of moisture on the rate of development of rancidity was included in this test. In detail the tests were as follows:

FIRST SET—A 20-cc. bottle was filled with lard, and a second one with lard in which three bright copper strips were placed. The bottles were corked and sealed.

SECOND SET—A 20-cc. bottle was filled with lard, and a second one with lard in which three bright copper strips were placed; 0.2 cc. of water was added to each, and they were sealed and well shaken.

THIRD SET—A 20-cc. bottle was filled with lard and a second one with lard in which three strips of copper were placed; they were allowed to remain open and exposed to the air.

FOURTH SET—A 20-cc. bottle was filled with lard and a second one with lard in which three copper strips were placed; 0.2 cc. of water was added to each, after which they were well shaken, and allowed to remain open and exposed to the air.

The lard used in all of the above tests was freshly rendered from leaf fat and contained 0.22 per cent of free fatty acids calculated as oleic acid. After filling, all bottles were placed upon a laboratory table directly below a window facing the east. They remained upon this table from June 13 to October 1, when they were examined.

FIRST SET—Sealed, no moisture.
Lard alone: Odor, good; Kreis test, extremely faint.
Lard and copper: Odor, good; Kreis test, extremely faint.
No change in acidity was found. Copper had not been attacked.

SECOND SET—Sealed, 1 per cent water.
Lard alone: Odor, good; Kreis test, negative.
Lard and copper: Odor, good; Kreis test, negative.
Copper showed no evidence of having been attacked. The acidity of the lard alone had increased to 0.44 per cent and of the lard with copper to 0.37 per cent, calculated as oleic acid.

THIRD SET—Open in air. No moisture.
Lard alone: Odor, rancid; Kreis test, intense.
Lard and copper: Odor, rancid; Kreis test, intense.
The lard of the lard and copper was green in color, showing that the copper had been attacked.

FOURTH SET—Open in air, 1 per cent water.
Lard alone: Odor, rancid; Kreis test, strong.
Lard and copper: Odor, rancid; Kreis test, intense.
The copper had been attacked, as was evidenced by the green color of the fat.

It is clearly evident from the foregoing tests that oxygen, either free or combined, is an essential in the production of rancidity in fats, whether metals or moisture, or both, be present. Further, direct sunlight and summer temperatures did not cause the production of rancidity in fats which were protected from the access of air. It will also be noted that of the fats in the sealed containers, those in which moisture was present became rancid somewhat more slowly.

PRODUCTION OF RANCIDITY IN CORN OIL AND COTTONSEED OIL AS AFFECTED BY METALS

SERIES V—Corn oil and cottonseed oil do not become rancid as rapidly as animal fats, perhaps on account of the fact that they contain glycerides of the lesser saturated fatty acids. To determine the influence of metals on the production of rancidity in these oils, the following test was conducted:

Cottonseed oil (20-cc. samples) was placed in each of seven 50-cc. glass beakers, and in each of six of these was placed a weighed 0.75-in. square of iron, lead, tin, zinc, copper, and aluminium, respectively. To the remaining beaker no metal was added. They were then allowed to remain for 3 wks. upon a laboratory table exposed to light, when the metals were removed and the loss in weight of each metal, the acidity, and the rancidity of the oil were determined. The results are shown in Table III.

At the same time and under identical conditions, similar tests were conducted with corn oil and lard. In the case of lard, however, changes in acidity were not determined.

The cottonseed oil (iodine value = 105.36; acid value = 0.17) and the corn oil (iodine value = 119.1; acid value = 0.86) were purchased in the open market and represent a good grade of the commercial product.

Rancidity failed to develop in any one of the three samples in which no metal had been placed, although the acidity of both the corn oil and cottonseed oil was slightly diminished. Of the samples of cottonseed oil in contact with metals, those in which iron, lead, and copper had been placed showed, by the Kreis test, marked rancidity, while the one with zinc gave only a slight positive reaction. The samples containing aluminium and tin, when subjected to this test, afforded a blue color, not before noted, but which, nevertheless, was regarded as due to the development of rancidity, or at least to a similar change in the fat. The acidity of all the samples of cotton-

TABLE III—EFFECT OF METALS ON PRODUCTION OF RANCIDITY IN COTTONSEED OIL AND CORN OIL[1]

		IRON			LEAD			COPPER			ZINC			ALUMINIUM			TIN			OIL OR FAT	
FAT OR OIL	Original Acidity	Loss Mg.	Acidity	Kreis Test	Loss Mg.	Acidity	Kreis Test	Loss Mg.	Acidity	Kreis Test	Loss Mg.	Acidity	Kreis Test	Loss Mg	Acidity	Kreis Test	Loss Mg.	Acidity	Kreis Test	Acidity	Kreis Test
Cottonseed	0.17	0.0	0.05	+2	68.3	0.62	+4	0.0	0.05	+5	1.4	0.11	+1	0.0	0.05	(Blue)	0.0	0.11	(Blue)	0.11	—
Corn	1.86	0.0	1.86	—	44.0	1.69	+1	3.1	1.18	+4	12.1	1.57	—	0.0	2.25	—	0.1	1.35	+3	1.69	—
Lard	..	0.0	..	+4	63.9	..	+5	0.0	..	+5	0.0	..	+3	0.0	..	+4	0.3	..	+3	..	—

[1] Three-week exposure.

TABLE IV—EFFECT OF COATINGS ON METALS IN PRODUCTION OF RANCIDITY

DATE 1912 8/1	Lard (Glass Cup)		Lard (Bakelized Tin Cup)		Lard (Tin Cup)		Lard (Bakelized Galv. Iron Cup)		Lard (Galv. Iron Cup)		Lard and Bakelized Copper (Glass Cup)		Lard and Copper (Glass Cup)	
	Odor	Kreis Test	Odor	Kreis Test	Odor	Kreis Test	Odor	Kreis Test	Odor	Kreis Test	Odor	Kreis Test	Odor	Kreis Test
8/6	—	—	—	—	—	—	—	—	—	+2	—	+2	—	+2
8/8	—	—	—	—	—	—	—	—	—	+2	—	+2	+1	+3
8/10	—	—	—	—	+1	+3	—	—	—	+2	—	+3	+1	+3
8/13	—	—	—	—	+2	+3	—	—	+1	+3	—	+3	+2	+4
8/15	—	—	—	+1	+2	+4	—	—	+2	+3	+1	+4	+3	+4
8/17	—	—	—	+2	+2	+4	—	—	+2	+4	+1	+5	+3	+5
8/20	—	—	—	+3	+2	+4	—	—	+2	+4	+1	+5	+3	+5
8/22	—	—	—	+3	+3	+5	—	—	+3	+5	+2	+5	+3	+5
8/24	—	—	—	+3	+3	+5	—	—	+3	+5	+3	+5	...	...
8/27	—	—	+1	+4	+3	+5	—	+1	+3	+5	(1)	...	...	...
8/29	—	+1	+2	+5	+3	+5	—	+2	+3	+5	...	...	...	...
8/31	—	+2	+2	+5	+3	+5	+1	+3	...	...	...	...	...	...

[1] Contained 1.2 mg. copper per 50 g. fat.

seed oil decreased with the exception of that of the oil in contact with lead. Lead in cottonseed oil lost 68.3 mg. in weight, and zinc 1.4 mg.; the other metals suffered no determinable loss. It appears from this that cottonseed oil in contact with metals develops rancidity more rapidly than cottonseed oil stored in glass alone, even when the metals suffer no apparent loss of weight.

Corn oil was not affected as much by contact with metals as was the cottonseed oil; only those samples in contact with lead, copper, and tin developed rancidity. Lead, copper, and zinc lost appreciably in weight; tin, but slightly, while iron and aluminium showed no loss. The original acidity of the corn oil remained unchanged in contact with iron, while in contact with lead, zinc, tin, and copper, and even in glass alone, decreased acidities resulted. The oil in contact with aluminium, however, increased in acidity. It appears that contact with metals promotes development of rancidity in corn oil. Some metals act more energetically than others, but in no case is corn oil as greatly affected as cottonseed oil under similar conditions.

All of the lard samples in contact with metals developed rancidity even when the metal itself was apparently not attacked, while rancidity did not develop in the lard not in contact with a metal.

It will be further noted that the oils in contact with copper developed rancidity more rapidly than those in contact with other metals; those in contact with tin and aluminium were the least affected.

THE VALUE OF PROTECTIVE COATINGS ON METAL IN PREVENTING PRODUCTION OF RANCIDITY

SERIES VI—As metallic containers for fats are by far the most common, having been found by experience to be the most adaptable, and as contact of metals with fats undoubtedly hastens the development of rancidity, an attempt was made to determine the influence of a protective coating of lacquer. The lacquer selected for this purpose was bakelite and was applied in the manner directed by the manufacturer; that is, the thoroughly cleansed metal was painted with the lacquer and, after being dried, was heated while under air pressure.

Copper, tin, and galvanized iron were employed in the test. Portions of lard (100 g.) were placed in a lacquered tin cup, in an untreated tin cup, in a lacquered galvanized iron cup, and in an untreated galvanized iron cup, all cups being of practically the same size. In the test with copper both lacquered and untreated copper strips of the same size and shape were submerged in separate 50-g. portions of lard contained in 100-cc. glass beakers. With 50 g. of the lard in a glass beaker as a check, all of the samples were placed upon a laboratory table exposed to the light, portions being removed from time to time by carefully melting, stirring, and withdrawing small equivalent amounts of the fat. The results of rancidity tests are shown in Table IV.

It will be noted that in each case rancidity developed earlier in the fat exposed to the unlacquered metal. The difference in the time of appearance of rancidity in the fat exposed with the protected and unprotected copper strips is very slight; however, the lard containing the protected copper strip showed at an early date the green color of copper soaps, and on analysis was found to contain 2.4 mg. of copper per 100 g. of fat, showing that the bakelite coating upon the strips was not intact.[5]

The greatest difference in the time of the appearance of rancidity is found in the case of the galvanized iron cups. In the unprotected galvanized iron cup, the lard was faintly rancid by the Kreis test on the sixth day, while the lard in the protected cup did not give a faintly positive Kreis test until between the twenty-seventh and twenty-ninth days; and, as the lard in glass showed a very faint Kreis reaction on the twenty-ninth day, the protective coating on the galvanized iron cup was evidently efficient.

In the tin cups, the lard in the unprotected cup showed a faint Kreis test on the sixth day, and in the protected cup, between the seventeenth and twentieth days.

These tests indicate:

1—The production of rancidity in fats is hastened by contact with metals.

2—A continuous and unbroken coating of lacquer upon a metallic container effectually prevents the effect of the metal in promoting rapid production of rancidity.

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[5] Copper strips lacquered with bakelite, immersed in lard, were kept exposed to air for several weeks at an elevated temperature of 70° C. with complete protection of the metal.

The American Relief Administration recently forwarded to Russia a consignment of scientific literature selected by various bureaus of the Department of Agriculture, for the purpose of supplying Russian men of science with the results of American scientific work accomplished since 1914. Since that time very few scientific publications from America have entered Russia. Arrangements were made through the American Committee to Aid Russian Scientists with Scientific Literature.

The Determination of the pH Value of Commercial Glucose as a Substitute for the Candy Test[1]

By Otto A. Sjostrom[2]

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In the following paper a simple method is given for the accurate determination of the actual acidity of glucose by means of colorimetric comparison with standards of known pH.

The difficulties and inconveniences connected with the use of the candy test as a measure of the inverting power of commercial glucose are pointed out.

The relation between the inverting effect of glucose as found from the candy test and the pH value for a definite concentration has been determined and expressed in the form of a curve.

COMMERCIAL glucose is used mainly for two purposes; for the mixing and blending of table sirups and for the manufacture of candy. Corresponding to these uses the glucose is manufactured and put on the market in two brands, mixing glucose and confectioners', or crystal, glucose. The mixing glucose is lighter, about 40° Bé., the gravity varying according to the season of the year and to the climate of the territory in which the table sirup is to be consumed. The crystal glucose is furnished in brands of definite gravity, from 42° to 45° Bé. The essential difference between these two brands is that of gravity. In one respect, however, the standards of quality are more definite for the crystal than for the mixing glucose and that is in regard to the acidity of the finished product.

As is well known, dextrose is readily decomposed by the action of even very small amounts of alkali and a slight acidity is therefore essential to the keeping quality of glucose. This acidity is of no detriment in the mixing glucose and might even be considered beneficial, as it promotes the inversion of the cane products with which the glucose is blended. But in the case of crystal glucose an excess of acidity, even if slight, over a certain limit established on the basis of practical experience is detrimental to the quality of the product from the candy-maker's point of view. When in the manufacture of candy glucose is boiled with cane sugar, inversion of the latter takes place to an extent determined by the acidity of the glucose. A small degree of inversion does no harm and is possibly desirable in some cases, but when the formation of invert sugar goes beyond a certain limit the quality of the candy suffers; this applies particularly to the different kinds of so-called "hard candy." The candy becomes hygroscopic or, to speak with the candy-maker, "sticky" very easily. This is due to the presence of levulose, which is more hygroscopic than the other sugars. Of course, under certain conditions of temperature and humidity all candy will become "sticky." There are no particular standards to meet in this respect but the candy-maker knows by experience how much the candy can be expected to stand under certain atmospheric conditions, and when the candy is "out of the ordinary" he lodges a complaint with the glucose manufacturer.

The acidity of glucose is low, usually about 0.01 per cent expressed as HCl, using phenolphthalein as indicator. This acidity is due to acid phosphates and organic acids which are present in varying amounts. It is natural that there should be certain fluctuations in the acidity of the finished batches of glucose, due to varying conditions in the different stages of a rather complicated manufacturing process and sometimes to differences in the raw material of manufacture. The most convenient way of keeping track of the acidity would of course be to determine the same for each batch by titration, but while this is always done as a matter of record it has long been known that the titration is not a sufficient or correct index of the suitability of glucose for the candy manufacturer. The practice has therefore been to apply a test to the glucose which imitates the conditions under which the product is to be used. This "candy test" is carried out in the following manner:

> Glucose, cane sugar, and water in definite proportions are heated in a copper pan at such a rate that the temperature of the mixture reaches 320° F. in 25 min. The contents of the pan are then poured out on a marble slab and left to cool. All operations are carried out according to detailed and rigid instructions. A table showing the relation between temperature and time has to be followed to the second. After cooling, the candy is broken up, an average sample is taken, and from this sample 5 g. are weighed out and dissolved in a 100-cc. flask which is filled to the mark. In this solution the reducing sugar is determined in the ordinary way with Fehling's solution by titration.
>
> The reducing sugar found represents the sum of the dextrose from the glucose used in the test and the invert sugar formed from the cane sugar during the heating. For the sake of simplicity the reducing sugar is all counted as dextrose. The dextrose from the glucose can be calculated from the dry substance of the latter, and a table has been worked out which gives this dextrose as per cent of the total dry substance of the candy for varying purities. In another table the results of the titration for total dextrose are expressed as per cent of total dry substance. The difference between the latter value and the value found from the first table gives the amount of invert sugar in the candy. The permissible maximum of invert sugar has been fixed to 8.5 per cent, and any batch of glucose which gives a higher inversion is diverted to the table sirup department.

The candy test gives also important information about the quality of the glucose in other respects, when interpreted on the basis of practical experience. It is therefore indispensable to the glucose manufacturer.

For general information about the quality of the glucose occasional tests are sufficient. But for information about acidity every batch has to be tested, if the record is to be kept complete, and with only this test available the control work becomes quite a problem for the laboratory, especially if the output of the plant is large.

The test is cumbersome and time-consuming and requires the undivided attention of the operator, who consequently can attend to only one test at the time. The least carelessness on the operator's part results in incorrect data on the acidity effect, as the degree of inversion is very sensitive to any deviation from the time-temperature schedule and the analytical part has to be carried out accurately to give reliable results.

Hydrogen-Ion Measurements

It occurred to the writer that sufficient information about the inverting power of glucose could be gained in a much more simple and rapid way by applying some of the principles of physical chemistry to this problem. The varying quantities of organic and inorganic acids in the glucose determine the degree of inversion by virtue of the concentration of the hydrogen ion to which they give rise. The methods for the determination of this concentration have been worked out carefully and are finding widespread industrial application. The investigation was therefore a matter of determining the pH values of a number of glucose samples, the inversion figures of which were known from the candy tests, and expressing the connection between these values in the form of a curve.

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[1] Presented before the Division of Sugar Chemistry at the 63rd Meeting of the American Chemical Society, Birmingham, Ala., April 3 to 7, 1922.

[2] Research Chemist, Corn Products Refining Company.

Both the colorimetric and the electrometric method have been used. The latter, of course, has its place in an investigation of this nature; but for routine work the colorimetric method is the only one to be considered. It is simple, rapid, quite accurate, if carried out with due attention to details, and—last but not least—almost foolproof.

The pH values of glucose solutions, under the conditions of test which will be spoken of later, range between 3.5 and 5.5 pH. For standard solutions covering this range either the Sorensen citrate mixtures or the more recently suggested phthalate mixtures can be used. The writer from long familiarity prefers the former and cannot find that the latter offer any advantages, in spite of claims for greater convenience in preparation. Besides, citric acid is cheap and can easily be obtained in sufficiently pure quality.

The composition of the citrate mixtures for different pH values is given in Clark's well-known treatise.[3] However, the intervals of pH in Clark's table are quite irregular and considerable interpolation is necessary to find the relations for increments of 0.1 pH. The writer has therefore used the excellent diagram found in Michaelis's book,[4] from which a table can be made up covering the desired range.

The indicator which covers most closely the range in this work is methyl red. For acidities in the vicinity of and above 4.0 pH bromophenol blue would be more convenient, as in this part of the range the color changes of the latter are much more marked than those of methyl red. Besides, bromophenol blue is very permanent, whereas the methyl-red colors fade rather rapidly and can be used only for immediate readings, within half an hour after addition. The great difficulty with bromophenol blue is, however, that the color which it imparts to glucose solutions is of a different quality from that of a standard solution of the same pH. The main difference seems to be that the red is more strongly absorbed in a glucose solution, so that the latter in daylight appears blue, whereas a standard solution is purplish blue or violet. Clark, in the chapter on "Optical Aspects," discusses this phenomenon as observed in turbid solutions with bromophenol blue and suggests the use of a light screen of a certain quality in order approximately to equalize the colors. Accordingly, various screens were tried, but in the case of glucose the difference in color character is so great that it was not possible to devise an arrangement for the equalizing of the colors without at the same time reducing the sensitiveness of the method too far for accurate color comparison. It might be mentioned that by working with electrometrical measurements as a guide the eye can be trained to these peculiarities, so that after some practice very close guesses of pH values can be made. Methyl red, however, gives practically the same hue of color with glucose solutions as with the standards and the color changes are sufficiently marked to allow determinations to 0.1 pH, although in the more acid part of the range the changes are of course in the color value rather than in the hue.

For the color comparison a simple comparator on the Walpole principle, such as the one recommended by Clark, answers all purposes. The comparisons are facilitated by the fact that glucose solutions are clear and not at all or very slightly colored. The work should be done in daylight and it is very essential to accuracy that the light be uniform. An excellent illumination for observations is the reflected light from a large plate of white enamel glass, of the kind commonly used for sanitary table tops, which is laid on a table close to a window. In this light all irregularities due to clouds in the sky are eliminated.

In this connection some points concerning the physiological side of color comparison should be mentioned which apply more or less to all colorimetric work. All individual color comparison is eminently a matter of rapid and concentrated action, especially when judging different values of the same color. It is in the first moment of vision that the eye perceives most sharply the difference between values. Prolonged observation only lowers the power of discrimination. The best way to observe is therefore to "flash" the colors. The comparator block is held in a tilted position with the field dark, and by a uniform angular movement of the hand the color disks are made to appear and disappear in the same manner as if a screen were raised and lowered over the observation holes. The operation is repeated as many times as necessary. By working in this way the eye also gets a short rest between each observation, and color values can be read with great accuracy and with very little tiring effect on the eye. Color fatigue from prolonged observation manifests itself in a peculiar way. At first there is a decrease in the power of discrimination; then a rather sudden change takes place into a gross irregularity of perception and the observations become entirely unreliable. Fortunately the eye recovers very quickly from a fatigue of this kind but in the meantime mistakes might easily have been made. It is therefore advisable to guard against errors from this source by making the observations in the manner suggested, by "flashing," especially in the range close to 4.0 pH.

COLORIMETRIC TEST OF GLUCOSE

The colorimetric test of finished glucose batches is made as follows: The samples are first diluted to 22° Bé. This arbitrary concentration has been chosen as a compromise, in consideration of the facts that on one hand the pH value is less influenced by other factors and consequently more representative the less the sample is diluted, and that on the other hand dilution is necessary in order to handle the samples in test tubes and get a uniform mixture with the indicator. A practical point of advantage in regard to dilution is that the gravity does not have to be exactly the same for every sample. The effect on the pH value of a variation of a few tenths on either side of 22° Bé. is so small that it can be neglected.

The comparisons are made on 10-cc. samples of glucose solutions and standards, to each of which exactly 0.2 cc. of a 0.02 per cent alcoholic solution of methyl red has been added. This amount of indicator was determined by experiment. When rather exact information on pH values is needed, as in this case, it is essential to establish as closely as possible that strength of color which will give the maximum of color differences for variations of pH. It was found that with the above amount a maximum of sensitiveness was attained. The strength of color for a given proportion between indicator and volume of solution depends of course upon the lumen of the test tubes used.

By carrying out the color comparisons in the manner described the pH values can be determined to 0.1 pH in the upper, more acid part of the series, and to 0.05 pH in the lower part. For ordinary routine work the standards are made up in increments of 0.2 pH and the pH values estimated to 0.1 pH.

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[3] "The Determination of Hydrogen Ions," p. 82.

[4] Michaelis, "Die Wasserstoffionen-Konzentration," p. 173.

COMPARISON WITH CANDY TEST RESULTS

The numerical relation between the inversion figures from the candy tests and the pH values for glucose diluted to 22° Bé. is shown in Fig. 1. The samples were selected according to candy tests already made and the figure represents the original data upon which the relation was based. From the difference in inversion results for the same pH value it can be seen that the candy test is far from reliable when made under conditions which require a comparatively large number of tests to be completed within a limited time. It is interesting to note that the points are grouped so as to form a sort of lane and are about equally distributed on both sides of this lane. The curve was therefore drawn through this lane and represents in an approximate way the average of these values. From a great number of additional comparisons in which the candy tests were made with particular care the relation between the values has been found to correspond fairly well to this curve, except in occasionally occurring batches of very high or low pH. Such batches give irregular inversion results. It happens occasionally that the candy test gives an inversion figure quite inconsistent with the pH value, but careful repetition of the test has shown every time that the first result was incorrect and due to an error of some kind in the work.

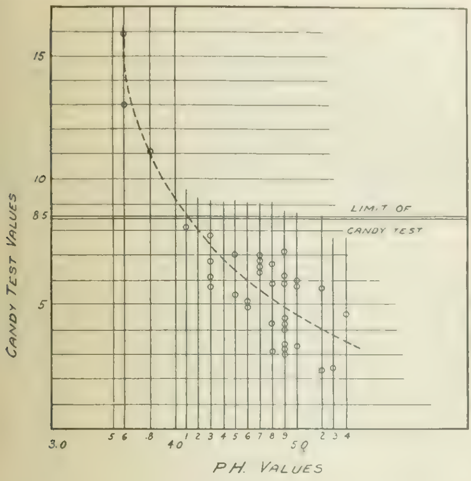

FIG. 1

TABLE I—RELATION BETWEEN pH VALUE AND INVERSION

pH	Invert Sugar Per cent
3.6	16–30 (irregular)
3.7	13
3.8	11
3.9	10
4.0	9.3
4.1	8.7
4.2	8.1
4.3	7.5
4.4	6.9
4.5	6.4
4.6	6.0
4.7	5.6
4.8	5.2
4.9	4.8
5.0	4.5

The average relation between pH value and inversion, as taken from the curve, is shown in Table I.

It has already been mentioned that the limit for invert sugar is set to 8.5 per cent of the total dry substance candy. According to Table I this corresponds to a pH value between 4.1 and 4.2. In order to be on the safe side we have made it a rule to consider 4.3 as the upper limit of acidity. A glucose of 4.3 or higher numerical value is passed without further test. If the value is 4.2, a careful candy test is made and the batch is passed or not, according to the result of this test. The general run of pH values is in the range between 4.5 and 4.9.

The relation which has thus been established between pH value and inversion may not hold in the same numerical way under all conditions, that is, with glucose of less uniform purity than the product manufactured at the plant where this investigation was carried out, or with glucose made under different manufacturing conditions. It is not likely, however, that the difference would be great, and it would at any rate be a comparatively easy matter to find the proper relation with the aid of the information given in this paper.

Note on the Use of the Mohr Pipet[1]

By Wayne D. Iler

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Having frequent occasion to use the Mohr pipet for small titrations, the writer has found the following device of great assistance, and as he has no recollection of having seen this particular application of an old device described in print, it is here given for what it may be worth.

A piece of rubber tubing about 4 cm. in length is slipped over the top of the pipet; a glass bead is placed in the tube, and a short, glass mouth-piece is fitted into the other end of the tube. A slight pressure over the glass bead with the thumb and forefinger allows the pipet to be filled or emptied, and it is readily cleaned after slipping the whole device off the pipet.

This device has the following advantages:

(1) It prevents the fatigue induced by holding the finger tightly over the top of the pipet.

(2) It makes no difference whether the fingers be wet or dry, whereas, in the ordinary manner of using the pipet, the finger and the top of the pipet must be reasonably dry.

(3) It makes possible a greater degree of accuracy in titrations, as the liquid is automatically held in the pipet until released by pressure on the rubber tube, and this pressure can be so regulated as to "split drops" with great ease.

(4) It is possible to make a series of small titrations with one filling of the pipet, as the pipet can be transferred from one hand to the other, or placed in a clamp-stand while recording results.

(5) In case the top of the pipet becomes broken or nicked, it is still possible to use it by means of this device.

To obtain satisfactory results, the bead must fit the rubber tube fairly tightly, and it may be found necessary to renew the tube frequently, but the writer has found the device very satisfactory, and well worth the small amount of trouble involved in keeping it in order.

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[1] Received June 1, 1922.

Cactus as a Fodder

In those parts of the country where, in the neighborhood of sugar factories, wide areas of land overgrown with cactus are available, the slicing machine and the pulp drier at the sugar works may be used for converting the cactus into a fodder.

The cactus is exposed to a torch to burn the thorns away and then carried to the slicing machine with specially formed knives. These slices are then dried, and if desired they may be ground to a coarse powder. During the slicing part of the juice is pressed out and may be collected separately. It can be converted to a substitute of gum arabic, which is probably a salt of the meta-arabic acid. The yield of dry material is about 11 per cent of the raw cactus.

Sugar Purity Determinations[1]

By **W. D. Horne**

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The following paper describes a method of making sugar purity determinations which can be carried through in not over 60 per cent of the time required for the wet lead method.

The paper describes a special spindle for making Brix determinations in which temperature corrections can be read directly from the instrument. Clarification is accomplished with a specially prepared dry lead powder, eliminating the measurement of exactly 100 cc. and dilution to exactly 110 cc. The paper ends with the description of a table for reading sugar purities, knowing Brix value and polarization. The method eliminates several common sources of error, thus improving quality as well as quantity of the work done in the sugar laboratory.

IN SUGAR manufacture and refining no analytical determination is of such importance as that of the purity. All massecuites are adjusted in purity to the proper degree so that the desired quality of sugar may result, the proper yield be obtained, and the treated material fit in as it should with what precedes and what follows it. Sirups or molasses must be tested for purity to determine that the proper ratio exists between them and the massecuites from which they spring.

A useful factor is the concentration of impurities in sirup as compared with that in the massecuite. Of course, (100 − purity) gives the impurities, and it will be immediately apparent that the ratio of the impurities in the massecuite to the impurities in the sirup is a fairly constant factor for similar grades of massecuites. Since these factors progressively lessen as the purity of the massecuite goes down, it will be found a very useful aid in calculating the steps and yields in any proposed procedure in purification by crystallization.

Liquors from boneblack filters must be watched carefully as to purity to allow of proper segregation. So must sweet waters from bags, presses, char filters, or other source, in order to control operations and distribution. Raw sugar affination must also be very closely checked by purity determinations in order to insure sufficient, and to prevent excessive, washing in the centrifugals.

In a large plant, purity determinations form the main guide for chemical control and mount into the hundreds daily. The tests must be made quickly and with such accuracy as is compatible with speed. The procedure must be made as simple as possible.

Calculation of Purity

The two requisites to calculate the purity of a sample are its percentage of solids and its percentage of sugar. When the solids are determined by evaporation and the sucrose by double polarization, the purity obtained is known as the true purity; when the solids are determined by the gravity of the solution, whether through the pycnometer, the hydrometer, the Westphal balance, or the refractometer, and the sugar by single polarization, the result is called the apparent purity. This is the usual test and there are several ways of performing it. By Schmidt's method, largely used in European beet practice, the density of the solution is determined by a Brix hydrometer, the temperature correction noted, a portion of the solution clarified with subacetate of lead solution and polarized, and the sugar determined from a table giving the percentages of sugar for the various degrees Brix and the various polarizations. The ordinary polarization thus found is divided by the Brix, uncorrected for temperature, to find the apparent purity.

In Casamajor's method the calculation is modified so as to give the apparent purity directly without the intermediate finding of the percentage of sugar in the solution, for in ordinary house control the purity is the figure needed. Casamajor developed the formula:

$$\frac{26.048}{\text{Degree Brix} \times \text{specific gravity}} = \text{Factor}$$

This factor, multiplied by the polarization, gives the apparent purity. Such factors, calculated for the various degrees Brix and the intermediate tenths, are arranged in a table for ready use, and a further development consists in a table or set of tables giving the corresponding apparent purity for every tenth of a degree Brix and each tenth of a degree polarization.

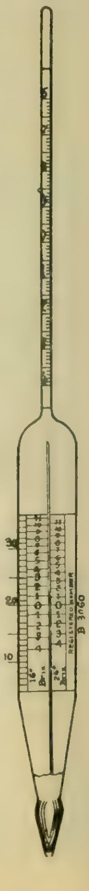
Some operators take the time and trouble to bring the solution being tested to the normal temperature before determining the degree Brix. If such a solution is also polarized at the same temperature, no error due to effects of changing temperature upon density and specific rotation can creep in. As the errors in polarization are very small for a slight temperature range, they are generally neglected, on account to the great inconvenience and loss of time incurred in bringing solutions exactly to a normal temperature.

The usual manner of determining the apparent purity is to find the degree Brix with a hydrometer in a tall glass cylinder, to observe the temperature of the solution, to clarify the solution with subacetate of lead, filter and polarize, and to calculate the purity from the corrected Brix and the observed polarization.

Rapid Determination of Purity

The following method developed by the writer for obtaining results rapidly and simply may be of use to others.

Density—For rapid Brix determinations a specially constructed spindle, which combines several novel features, has been evolved. The spindle is about 30 cm. over all, with a stem about 15 cm. long. This contains a scale of about 11 cm., covering 8 full degrees divided into tenths, each of which is just about equal to the depth of the meniscus of the solution. The lower part of the spindle is made almost plainly conical to give greater strength in resistance to breakage,



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[1] Presented before the Division of Sugar Chemistry at the 63rd Meeting of the American Chemical Society, Birmingham, Ala., April 3 to 7, 1922.

TABLE OF SUGAR PURITY

Brix. . . .	15.1	15.2	15.3	15.4	15.5	15.6	15.7	15.8	15.9	16.0	16.1
(Factor) . .	(1.6221	1.6108	1.5996	1.5887	1.5777	1.5670	[illegible]	[illegible]	[illegible]	1.5253	1.5152)
Pol.											
25.0	40.55	40.27	39.99	39.72	39.44	39.18	38.91	38.65	38.39	38.13	37.88
25.1	40.71	40.43	40.15	39.88	39.60	39.33	39.07	38.80	38.54	38.29	38.03
25.2	40.87	40.59	40.31	40.04	39.76	39.49	39.22	38.95	38.69	38.44	38.18
25.3	41.04	40.75	40.47	40.19	39.92	39.65	39.38	39.11	38.85	38.59	38.33
25.4	41.20	40.91	40.63	40.35	40.07	39.80	[illegible]	39.26	39.00	38.74	38.49
25.5	41.36	41.08	40.79	40.51	40.23	39.96	39.69	39.42	39.16	38.90	38.64
25.6	41.52	41.24	40.95	40.67	40.39	40.12	39.84	39.57	39.31	39.05	38.79
25.7	41.69	41.40	41.11	40.83	40.55	40.27	40.00	39.73	39.46	39.20	38.94
25.8	41.85	41.56	41.27	40.99	40.70	40.43	40.16	[illegible]	39.62	39.35	39.09
25.9	42.01	41.72	41.43	41.15	40.86	40.59	40.31	40.04	39.77	39.51	39.24
26.0	42.17	41.88	41.59	41.31	41.02	40.74	40.47	40.19	39.92	39.66	39.40
26.1	42.33	42.04	41.75	41.47	41.18	40.90	40.62	40.35	40.08	39.81	39.55

to increase the area of the thermometer bulb, so as to quicken its action, and to give ease in washing and wiping this part of the instrument. A new departure has been made in the scale of this thermometer. Centigrade degrees are shown from 10° to 35°, with 20° taken as the normal temperature, so as to cover all practical ranges, but these degrees are marked off well to one side. Immediately adjacent to the mercurial column are two direct temperature correction scales, showing in tenths of a degree Brix the temperature corrections to be added to or subtracted from the direct readings on the Brix scale. On one side of the mercury column are the temperature corrections applicable for density at the top of the Brix scale; on the other side are the corrections for readings at the bottom of the Brix scale. These corrections differ quite materially, so that a single temperature correction scale is very deceptive and leads to considerable errors in purity determinations. An interesting thing about this "Complete Temperature Correction Scale" is its rapid visibility, for just as one measures at a glance the relative position of the level of the liquid between the top and bottom of the Brix scale, so he intuitively arrives at the corresponding point between the maximum and minimum temperature corrections, which is to be taken and applied to the particular density reading obtained. In practice the matter is very simple, for usually the Brix is made up arbitrarily to lie quite near one end of the scale. An 8 to 16 Brix spindle is used for the general run of solutions that are rather dark and readings are taken between 15 and 16 Brix, while for lighter colored solutions a 16 to 24 spindle is frequently employed, and solutions are prepared to be read at the end representing the greater density.

Readings are always made to the closest half-tenth, and where unusual accuracy is desired the readings can be made to about a hundredth of a degree by interpolation. Equally close readings can be made on the temperature correction scales.

CLARIFICATION—The density having been obtained, the next operation, that of clarifying the solution for polarization, is greatly expedited by the use of the author's "dry lead" method, in which specially prepared anhydrous lead subacetate is employed in place of basic lead acetate solution. As this dry powder effects the same clarification without producing any alteration in the concentration of the sugar solution, the tedious and frequently inaccurate method previously followed can be greatly simplified. Instead of measuring off 100 cc. of the solution, adding lead solution and making up to 110 cc. with water before filtering, one simply throws out all but about 100 cc. of the sugar solution from the Brixing cylinder, adds with a little scoop a small amount of the "dry lead" powder, sufficient to cause flocculation (each 0.1 cc. of the dry lead is equivalent to 2 cc. of a 28° Brix solution of the subacetate), turns the cylinder over two or three times, and pours all directly upon a filter paper.

Since no correction need be added to the polarization, as was formerly the case to compensate for the dilution of the solution, a source of frequent error is eliminated.

POLARIZATION—For polarizing, a continuous tube is a convenience and saves time, and is good if the solutions are of nearly the same density, but when the densities of successive solutions change as radically as they do in refinery practice, the intermittent tube is safer. Covering ends that slide on, however, are to be preferred to those which have to be screwed on.

CALCULATION—There remains only the calculation, either by multiplying the polarization by the factor corresponding to the Brix, or by determining the product in some easier way. Various tables and a number of mechanical devices have been constructed for aiding in this operation. The one which the writer has found most convenient for the great majority of solutions tested is a long narrow table of figures giving all the purities corresponding to the different tenths of a degree Brix between 15 and 16 Brix or between any other two consecutive degrees, and the different tenths of a degree by the polariscope. The Brix readings head the vertical columns, while the polariscopic readings stand opposite the horizontal rows of figures. Such a table is about 25 cm. wide and nearly a meter and a half long. This would be quite unwieldy if it had to be used fully extended, and it would be a little inconvenient and subject to excessive wear if it were divided into pages in book form.

A very convenient arrangement which was devised many years ago, however, has proved fully satisfactory. The long paper strip is mounted on two wooden cylinders about 10 cm. in diameter and a little longer than the width of the paper strip. An end of the paper is tacked to each cylinder, and the cylinders are rolled until about half of the strip is wound upon each cylinder and a plane 20- to 22-cm. stretch of paper stands between the two. In this position the whole is mounted in a glass-fronted box and set up in a convenient position for the operator to use. Prior to assembling, each cylinder is bored out longitudinally and a Hartshorn spring shade roller inserted in each, in opposite directions and with ratchets removed. Each spring is given a fairly good tension, so that they tend to pull the two ends of the panoramic roll away from each other, and the whole system remains in practical equilibrium, no matter to which position the paper sheet may be brought. A small windlass handle protrudes from the center of the end of one of the cylinders through the side of the encasing box, so that the operator easily gives it a turn or two so as to expose whatever part of the table he wishes to bring into view.

This device gives great satisfaction to the operators and appears to have suffered no appreciable deterioration after long years of constant use. A part of the table of sugar purities is shown herewith.

According to *Drug and Chemical Markets*, the British dyestuffs licensing committee proposes to support the domestic dye industry by refusing import licenses when domestic dyes are available in adequate quantities and at reasonable prices. Reasonable prices are considered to be three times the pre-war prices of dyes in general. With regard to vat dyes, reasonable prices for indigo dyes will be two and one-half times and for other vat dyes, five times pre-war prices.

The Precipitate Formed in Sugarhouse Sirups[1]

By J. F. Brewster and W. G. Raines, Jr.

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COATES and Slater[2] in 1916 published a study of the precipitate that forms when clarified cane juice has been evaporated to sirup and allowed to stand. These authors examined two lots of precipitate obtained from two different Louisiana sugarhouses, where plantation white sugar was being manufactured by the sulfitation process. Of the organic constituents of their precipitates Coates and Slater isolated cane wax and found to be present a levorotatory substance which was not sugar. The percentages of ash in their precipitates were 58.0 and 75.6, respectively. The constituents of the ash reported were copper, oxides of iron, aluminium, calcium and magnesium, silica, sulfur trioxide, and phosphorus pentoxide. Coates and Slater conclude that, although the precipitate is made up of substances insoluble in the ordinary sense, it is held in colloidal solution by the heavy sirup, from which it flocculates on standing, particularly when kept hot.

Last year the present writers[3] analyzed a sirup precipitate resulting after cane juice had been treated with Filter-Cel and Norit. The ash analysis showed the presence of manganese in addition to the constituents found by Coates and Slater. A thorough study of a similar precipitate has been published very recently by Birckner,[4] who reported the presence of zinc in addition to the ash constituents enumerated above.

The fact that precipitation invariably occurs in sirup from cane, no matter how brilliant the clarified juice may appear before evaporation, and the fact that it is impossible to obtain high-grade white sugar unless the precipitate is removed, thus forming a distinct step in the process, makes its study important.

The source of the inorganic part of the precipitate-forming substances seems to be an open question. Coates and Slater conclude that the character of the precipitate varied according to the method of clarification. Birckner believes this to be true to a certain extent, particularly in those methods of clarification in which lime is used. The latter author, however, believes that in view of the occurrence of the precipitate in sirups resulting from treatment of juice with kieselguhr and Norit, that is, from treatment without the use of chemicals, it is doubtful whether the precipitate can be attributed, in its main features, to factors not inherent in the cane juice itself.

In [illegible] small-scale clarification experiments, we had as one object to determine whether it would be possible to remove precipitate-forming substances or to reduce the amount of precipitate formed. Cane juice in 10-liter lots was clarified, filtered by means of the laboratory press, and evaporated *in vacuo* to 30° Bé. while warm. The sirup was allowed to stand, and when the precipitate had settled the clear sirup was drawn off by suction and the residue stirred with water and centrifuged. The precipitate was washed three times by centrifuging with water, then thrown upon a filter and washed in the ordinary way until free from soluble matter. It was then dried at 100° and analyzed. As the methods of clarification differed, no refinements in analytical methods were attempted. The dried samples were ashed and after obtaining the weight of ash the latter was fused with sodium carbonate and the methods of silicate analysis applied. No attempt was made to separate the constituents of the ammonia precipitate, which may have contained some phosphates and members of the alkali earth groups. The results for determination of total precipitate and ash are shown in the following table.

The methods of clarification in the first column should be be explained. Under the head "sulfur-lime" in Expt. 1, is meant that the raw juice was treated with sulfur dioxide to an acidity of 5.0 cc. and limed back to neutrality against phenol red. The mixture was heated to the boiling point and filtered. The brilliantly clear filtrate was immediately evaporated. In Expt. 2 filter-paper pulp was mixed with the juice, heated, and pumped through the press. The paper proved to be a poor filtering medium when used in this way, the filtrate being cloudy. Norit alone was used in Expt. 3, giving a slightly cloudy filtrate. In Expt. 4, 2 per cent of freshly precipitated and thoroughly washed calcium carbonate was mixed with the juice, heated as in the other experiments, and filtered. The filtrate was brilliant and it was found that the acidity of the juice had been reduced about 50 per cent. Calcium carbonate is an excellent filtering medium and can be used in much less quantity than we employed here. Its use was suggested to us by Dr. Sauer, of the Norit Co., who had tried it previously as a possibility for direct manufacture of white sugar in conjunction with Norit. Expt. 5 was limed to neutrality (phenol red), 0.5 per cent of Filter-Cel added, heated, and filtered. The filtrate was clear. Expt. 6 represents juice limed to neutrality, heated, and filtered. In spite of difficulty in filtering, this mixture was all put through the press, although the filtrate was slightly cloudy. Expt. 7 was a precipitate obtained from the sugarhouse sirup tanks. This juice had been clarified with Filter-Cel, then decolorized with Norit in the presence of a small amount of added phosphoric acid which was neutralized with lime just before filtering. It

PRECIPITATES FROM SIRUP

Expt. No.	Clarification Method	Ppt. G.	Ash G.	Ash Per cent	Analysis of Ash, Per cent: SiO_2	Ammonia Ppt.	CaO	MgO	SO_3	P_2O_5
1	Sulfur lime	[illegible]	3.7121	87.32	23.23	1.11	32.02	None	42.00	0.46
2	Paper	[illegible]	2.2161	63.46	9.99	4.13	38.28	None	34.09	0.73
3	Norit		0.5808	. .	26.12	35.97	14.94	1.92	1.67	12.71
4	[illegible]		0.0838	. .	53.58	0.24	40.57	None	6.67	3.34
5	Lime Filter-Cel	0.3370	0.1627	48.28	37.95	25.47	26.35	None	1.63	None
6	Lime	[illegible]	0.5315	64.48	60.82	8.10	....	....	....	....
7	Filter-Cel Norit	[illegible]	1.1260	74.47	43.47	2.94	22.72	None	27.48	None

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[1] [illegible] Chemistry at the 63rd Meeting [illegible] Birmingham, Al., April 3 to 7, 1922.

[2] [illegible]

[3] [illegible] 13 [illegible]

[4] [illegible]

is to be noted that no phosphoric acid was found in this precipitate.

The cane used in the first six experiments had been windrowed under several inches of earth to preserve it. In Expts. 1, 2, and 3, the cane was unwashed and a considerable amount of adhering soil went into the juice. In Expts. 4, 5, and 6, the mud had been thoroughly removed by washing. Although the figures of the table are incomplete with regard to dry matter of precipitates in 3 and 4, it is easy to draw conclusions from the figures for quantity of ash. The outstanding feature seems to us to be the differences to be noted in total dry matter and ash in the washed and unwashed cane.

Attention should be drawn to the ash content of Expt. 3, where Norit was used on unwashed cane, and the ash content of Expt. 6, where lime only was used upon unwashed cane. Norit was an excellent adsorbent, while the quantity of lime used was too small to be considered of much aid in filtering. The balance is still slightly in favor of the washed cane. The washing of cane before crushing is practiced at many Louisiana sugar factories. One factory, at which this practice had been in force for 4 or 5 yrs., reported in 1919[6] that the volume of filter-press mud had been reduced 25 per cent. Filter-press mud carries away as much as 6 per cent of sucrose. No mention is made in this report of the influence of cane washing upon the amount of sirup precipitate. The question of sirup settling, however, is discussed and the difficulty of filtering sirup is mentioned. There can be little doubt in view of our results that the presence of adherent soil upon cane would have a great influence upon the quantity of sirup precipitate formed. This is not surprising when it is considered that soil may contain much matter, both organic and inorganic, in the colloidal state which could readily escape removal by our present clarification methods, including those in which highly adsorbent carbons are employed. It is evident that the formation of precipitate may be attributed to three possible sources—namely, from materials used in clarification, particularly in clarification by means of chemicals as suggested in the article of Coates and Slater, from substances present in cane juice itself, as suggested by Birckner and as substantiated by our results with washed cane, and finally from soil adhering to the cane at the time of crushing.

The amount of precipitate that one may obtain from sirup cannot be predicted from the appearance of the filtered juice or sirup. The filtrates and sirups in Expts. 1, 4, and 5 were clear. Those in Expt. 2 were very turbid, while in Expts. 3 and 6 the liquids were slightly cloudy. In some cases the precipitate had a tendency to fall readily after evaporation and in others there was no precipitation until the sirup had been heated to nearly 100° C.

As pointed out by Coates and Slater, filtration of the sirup for the removal of turbidity or precipitate would be too costly and troublesome, and settling appears to be the most feasible method of handling such sirup. It should be added that even when decolorization with carbon is performed at the sirup stage, a precipitate is to be found in the decolorized product. The precipitate analyzed by us last year resulted from such treatment. There is the possibility, of course, that to some extent precipitate-forming substances may be derived in the colloidal state from the so-called inert filtering media. With settling as the most feasible means of dealing with sirup precipitate, it becomes obvious that two conditions are to be sought. These are rapidity of settling and compactness of sediment. This suggests that the addition to the sirup, after it has been run to the settling tanks, of some adsorbent heavy enough to quickly subside and carry suspended matter with it, might answer the purpose. Fuller's earth, precipitated chalk, and calcium phosphate are substances we have tried and which show promise in this connection.

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[6] *Louisiana Planter*, **62** (1919), 187.

A Prescription for Hale, Hearty Life

By H. W. Jordan

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Each October we are confronted by the choice of wasting the year's two hundred long, cool evenings in aimless, casual entertainment, or of devoting them to wholesome recreation, balanced by sound reading and study. Repeatedly we see men past fifty, retired from active business by choice or circumstance, who mysteriously fade and soon die. Investigation usually discloses the fact that the victim had no impelling mental interest outside of business routine. Like all complex apparatus shut down or thrown on the scrap heap, he quickly disintegrated. Psychologists have proved that we must grow or go. Post-mortem examination of our friend's mind reveals the reason of his going. He had ceased to grow. He knew only one subject, his daily vocation.

Among ways of attaining active age none is better than to hold oneself rigidly to an annual program of reading, designed to impel creative thought. Not the habit of nightly wading through thirty-two pages of the metropolitan daily, an action interspersed with naps and subconsciousness, barely aware that we are momentarily hibernating until aroused by a tearful voice, "Mercy, it's twelve o'clock. Aren't you ever coming up, dearie?" Instead, a program of three to ten hours weekly devoted to earnest study of a group of subjects wholly outside personal business—history, travel, science, art, or music—to educate, to draw us out of and beyond our technical horizon.

If one seeks examples of such use of spare time he only need scan the biography and books of Theodore Roosevelt or Lord James Bryce to learn the unbelievable extent to which busy, practical men can carry systematic reading, and the value of the knowledge they thus acquire.

This century is destined to be characterized by enormously increased, practical understanding of the human mind, just as the nineteenth century was by colossal applied knowledge of material forces. Exceptional profit and marked individual success is to be won in commerce and engineering industry by correct application of laws which govern the human mind, as inexorably as gravitation and atomic weight rule material action. The Rockefellers and Carnegies of 1950–75 will be industrial executives who have correctly applied this new knowledge of man's mind to the greatest good of the greatest number.

A new, extensive literature has sprung up as a result of the war. It is devoted to the psychology of industrial social life, to a new interpretation of the Golden Rule which is the law of equal action and reaction, to the biology and evolution of states and nations, to mathematical analysis of conservative investment, and to the ebb and flow of mass mind in the seething action of industry and government. Among its authors are Edwin Grant Conklin, Madison Grant, Lothrop Stoddard, Walter Lippmann, Raymond Pearl, James Harvey Robinson, Arthur Pound, Norman Angell, Glenn Frank, Roger W. Babson, Dr. Coué, the French medical psychologist, Anatole France, Walther Rathenau, Guglielmo Ferrero, and John M. Keynes. Their books and their articles in our current magazines need be incorporated in our chemical and engineering subconsciousness. If you would be hale and hearty, devote the winter evenings of 1922–23 to the works of these writers.

Ethyl Alcohol from Western Larch—*Larix occidentalis,* Nuttall[1]

By E. C. Sherrard

Forest Products Laboratory, Department of Agriculture, Madison, Wisconsin

A method is given for the fermentation of 70 to 80 per cent of the total sugar resulting from the acid hydrolysis of western larch. This method is equally satisfactory for the fermentation of galactose alone.

Alcohol yields are given both for the water extract and for the solution obtained by the hydrolysis of the wood.

In 1916 Schorger[2] called attention to the presence of a water-soluble substance, galactan, in western larch. This material constitutes from 8 to 17 per cent of the wood and upon treatment with dilute acid hydrolyzes to give galactose. Schorger established its identity by several means but was unable to obtain a satisfactory fermentation; the best results obtained indicated a yield of about 40 per cent of alcohol when "S. Carlsbad I" yeast was used.

Because of the large quantity of hexose sugar preëxistent in the wood, Kressman[3] concluded that western larch would be one of the most valuable raw materials for the production of ethyl alcohol. He hydrolyzed the wood and obtained yields of total reducing sugar that corresponded to 26.21 to 30.52 per cent of the original material. His fermentation experiments showed, however, that, while the sugars resulting from the hydrolysis of the cellulose were removed, the galactose remained practically unchanged.

A means of completely fermenting galactose is highly desirable, not only because of the high content of hexose sugar in western larch, but also because of the large quantities of available waste. In addition to mill waste, such as sawdust, shredded slabs and edgings, a certain logging waste is encountered in the woods, owing to the fact that the butt logs produce an inferior grade of lumber and are so heavy that they prevent rafting. As a consequence, many of these logs of high galactan content are left in the woods. Since the butt logs contain the greatest amount of galactan (10 to 25 per cent) found in the tree, they constitute one of the best sources of this material. Other species of coniferous woods yield an average of 22 per cent total reducing sugar upon hydrolysis with dilute acid, so it is evident that if a similar quantity of sugar is obtainable from larch cellulose in addition to that contained in the galactan this wood should be an excellent source of ethyl alcohol.

EXPERIMENTAL

In order to study the fermentation of these sugars more readily the work was divided into three parts. In the first case the galactan was extracted from the wood with hot water, and then hydrolyzed by boiling for 4 hrs. after the addition of a sufficient quantity of sulfuric acid to make a 4 per cent solution. The galactose solution was then neutralized with calcium hydroxide and evaporated under reduced pressure until a solution was obtained that contained about 5 per cent total reducing sugar. This solution was then fermented as described below.

In the second experiment the residue remaining after the water extraction was hydrolyzed in the usual way, *i. e.,* it was digested in an autoclave for 15 min. at 115 lbs.' steam pressure with a quantity of sulfuric acid corresponding to 1.8 to 2.5 per cent of the dry weight of the wood. The wood was moistened with one and a quarter parts of water in order to insure a complete reaction. The resulting sugars were then extracted with water, the sulfuric acid neutralized with calcium hydroxide, and evaporated as before after the removal of the calcium sulfate by filtration.

In the third experiment the unleached larch was hydrolyzed under the same conditions as stated above, and the sugars extracted and prepared for fermentation in the same way as before. The sugar yields and fermentation data are set forth in the accompanying table.

SUGAR AND ALCOHOL YIELDS

Expt.	Treatment	Total Reducing Sugar Per cent	Total Sugar Fermentable Per cent	Theoretical Alcohol Per cent of Dry Wood	Actual Alcohol Per cent	Fermentation Efficiency Per cent	Alcohol Calcd. 95 Per cent per Ton of Dry Wood	Hydrolysis		
								Sulfuric Acid Per cent	Time	Pressure
I	Water-soluble portion	10.11	79	4.08	4.10	100.5	12.7	4	4	Atmos.
	Autoclaved residue	19.64	69	5.66	6.15	108.7	19.0	1.8	15	115 lbs.
	TOTAL	29.75		9.74	10.25		31.7			
II	Water-soluble portion A	12.37	75.4	4.76	4.69	98.5	14.75	4	4	Atmos.
	Water-soluble portion B	12.37	76.66	4.84	4.84	100.0	15.0	4	4	Atmos.
	Water-soluble portion C	12.37	80.50	5.09	5.09	100.0	15.8	4	4	Atmos.
	Water-soluble portion D	12.37	78.53	4.96	5.40	109.0	16.7	4	4	Atmos.
	AVERAGE	12.37	77.77	4.91	5.00	101.9	15.56			
	Autoclaved residue A	18.00	70.51	6.58	6.80	105.0	21.0	1.8	15	115 lbs
	Autoclaved residue B	23.07	70.02	8.25	8.99	109.0	26.2	2.5	15	115 lbs.
	AVERAGE	20.53	70.26	7.36	7.89	107.0	23.6			
III	Original wood autoclaved A	28.66	73.6	10.78	10.51	97.5	32.6	1.8	15	107 lbs.
	Original wood autoclaved B	29.35	72.0	10.78	10.78	100.0	33.4	2.5	15	107 lbs.
	AVERAGE	29.00	72.8	10.78	10.65	98.7	33.0			

Experiment I was a preliminary run to determine the most suitable conditions for carrying out the reaction. The sugar yields in all experiments are given as total reducing sugar in terms of glucose and were obtained by means of Fehling's solution with subsequent electrolytic deposition of the copper oxide. In Expt. II four check fermentations (A, B, C, and D) were carried out on the galactose solution. The yeast used in II-D had previously been used to ferment II-C which had, in turn, been obtained from the fermentation of II-B. With these exceptions, the experiments listed in the table were carried out with fresh yeast that had been propagated on malt mort.

The yeast used for the actual fermentation was a pure strain culture of a Hungarian beer yeast, *Saccharomyces*

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[1] Presented before the Section of Cellulose Chemistry at the 63rd Meeting of the American Chemical Society, Birmingham, Ala., April 3 to 7, [illegible] Department of Agriculture.

[2] [illegible] 8 [illegible]

[3] [illegible] 983

cerevisiae, which has been in use at the Forest Products Laboratory for several years and has proved very efficient in the fermentation of sugars resulting from the hydrolysis of wood.

The sugar solutions were prepared for fermentation by evaporating to a suitable concentration and then adding a sufficient quantity of 10 per cent solution of *autolyzed* yeast to make the whole correspond to a 2 per cent yeast solution. The yeast water was prepared according to the method of Fred and Peterson by boiling autolyzed yeast with distilled water for one hour and filtering while hot. The solution was then again boiled, filtered, and finally sterilized in an Arnold steam sterilizer.

Discussion of Results

In the fermentation of the sugars resulting from the autoclave cooks of the extracted residue no precautions are necessary other than those already described.[3] In order to obtain a satisfactory fermentation of the solutions containing galactose, however, it is imperative that the temperature and acidity be carefully regulated. The temperature must be held between 85° and 90° F., and the initial acidity of the solution not greater than 5°. If the acidity is greater little or no fermentation takes place. When the galactose solution is fermented alone, but very little increase in acidity occurs as the fermentation progresses, but when the solution resulting from the hydrolyzed wood is fermented, an increase of 4° acidity is quite common.

In view of the difficulty formerly encountered in the fermentation of galactose, it is quite surprising that such good results are obtainable under the conditions outlined in this paper. In all cases the fermentation took place better in the galactose solution than in the liquor containing the mixed sugars. In Expt. II the minimum total yield was 35.95 gal. of 95 per cent ethyl alcohol per ton of dry wood, while the maximum was 42.9 gal. The average yield from this was 39.9 gal., by far the largest yield of alcohol obtained from any wood. In Expt. III, in which the mixture sugars were used, the average yield was 33 gal. of 95 per cent ethyl alcohol per ton of dry wood. This lower yield is no doubt due to the greater acid-forming tendency of the sugars other than galactose, with a consequent inhibition of the yeast in the fermentation of the latter sugar. Even in this case the yield was almost 10 gal. greater than from any of the woods previously studied.

The fact that galactose from western larch can be fermented readily with the production of ethyl alcohol is particularly interesting from the standpoint of the paper-maker, since by an extraction of his chips with water before pulping a quantity of sugar is obtainable that is easily convertible into ethyl alcohol.

Radioactivity of Miscellaneous Waters Examined in the Bureau of Chemistry[1,2]

By W. W. Skinner and J. W. Sale

Water and Beverage Laboratory, Bureau of Chemistry, Department of Agriculture, Washington, D. C.

From the experience of the Bureau of Chemistry, in analyzing commercial bottled waters of natural origin, and from published data, it may be concluded that shippers of these products are not justified in making any statements on the labels which will induce prospective consumers to purchase the articles because of their radioactivity.

THE ENFORCEMENT of the Federal Food and Drugs Act of 1906 necessitates the examination of mineral waters and other products for content of radioactivity. Consequently the Water and Beverage Laboratory was equipped with three electroscopes of the emanation type, an alpha-ray electroscope, the apparatus designed by Boltwood[3] for separating and collecting emanation, and other apparatus necessary for making analyses of the radioactivity of various products. This equipment, the methods used in calibrating the electroscopes, determining the radioactivity of samples, and reporting results have been described in a previous communication[4] from this laboratory.

Foreign and domestic bottled mineral waters, pads, ointments, capsules, sediments, and other products classified as drugs, coming within the jurisdiction of the Act, are examined, if their labels bear statements relating to radioactivity. In addition to official samples of this nature, the laboratory has examined a few spring, river, lake, and ocean waters collected by Bureau representatives for the purpose of obtaining data for use in litigation.

In the examination of bottled waters, it is usually sufficient to determine the activity as received, in which case before removing the stopper the sample is chilled, opened, the contents acidified, and poured carefully into the boiling-out flask. Agitation of the water is avoided after the sample is received in the laboratory. Ordinarily, no attempt is made to determine the activity of the gas in the neck of the bottle, since only the emanation or radium salt, dissolved or suspended in the water, is consumed. As we have usually no knowledge of the exact time when the water is bottled, it is obviously impracticable to calculate the initial activity of the water at source by using the accepted formula which represents the rate of decay of emanation. We do make this calculation, however, on samples collected from source for investigation purposes when adequate precautions are taken. It is desirable sometimes to determine whether or not activity is due to the presence of radium salts dissolved or suspended in the water, in which case the permanent activity is determined in the ordinary manner.

In the accompanying table, the results have been expressed in grams of radium $\times 10^{-9}$ per liter, corresponding to activity found. This unit is known also as millimicrogram, and is one billionth of a gram. The letter I in the column of results means that the time of collection of the sample was known and the initial activity, I, of the sample has been calculated; R indicates that the value in the table represents the activity of the sample as received in the laboratory, which may or

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[1] Presented before the Division of Water, Sewage, and Sanitation at the 61st Meeting of the American Chemical Society, Rochester, N. Y., April 26 to 29, 1921.

[2] Published with permission of the Department of Agriculture.

[3] *Phil. Mag.*, [6] **9** (1905), 599; *Am. J. Sci.*, [4] **18** (1904), 378.

[4] "Determination of Radioactivity," *J. Assoc. Official Agr. Chem.*, **2** (1916–17), 116.

RADIOACTIVITY OF MISCELLANEOUS WATERS

No.	Type	Location	Date of Examination	Quantity of Water Used Liters	Grams Radium × 10^{-9} per Liter Corresponding to Activity Found
		[illegible] by a Bureau representative			
1	Cold spring	Virginia	Nov. & Dec. 1911	2.0 (approx.[5])	0.023 R; 0.05 I
2	Cold spring				0.062 R; 0.21 I
3	Cold spring				0.171 R; 0.21 I
4	Cold spring				0.062 R; 0.09 I
5	Cold spring				0.052 R; 0.06 I
6	Hot spring				0.232 R; 0.33 I
7	Hot spring				0.754 R; 1.10 I
8	Hot spring				0.167 R; 0.28 I
9	Cold spring				0.005 R; 0.007 I
10	Cold spring				0.043 R; 0.06 I
11	Cold spring				0.758 R; 0.93 I
		[illegible] at source by a Bureau representative			
12	Philadelphia tap water	Pennsylvania	June 1917	2.3	None or not more than 0.002 R
13	Washington tap water	Potomac R., D. C.	June 1917	2.3	Not more than 0.002 R
14	Reading tap water	Maiden Cr., Pa	May 1917	2.3	0.006 R; 0.002 P
15	Lancaster tap water	Pennsylvania	May 1917	2.3	None or not more than 0.002 R
16	Mississippi River	St. Louis, Mo., unfiltered	May 1917	2.3	None or not more than 0.002 R
17	Lake Michigan	Chicago, Ill	May 1917	2.3	None or not more than 0.002 R
18	Atlantic Ocean	4 mi. off Atlantic City, N. J.	June 1917	2.3	None or not more than 0.002 R
19	Lake Erie	4 mi. from Buffalo, N. Y.	June 1917	2.3	None or not more than 0.002 R
		Domestic bottled waters			
20	Cold spring[1]	Wisconsin	Sept. 1912	2.4	0.037 R; 0.063 I
21	Cold spring[1]	Wisconsin	Sept. 1912	2.4	0.038 R; 0.076 I
22	Warm spring[1]	Massachusetts	July 1914	2.4	0.188 R; 0.070 I; 0.002 P
23	Cold spring[1]	Massachusetts	July 1914	2.4	0.042 R; 0.183 I; 0.002 P
24	Warm spring[2]	Massachusetts	June 1915	2.4	None or not more than 0.002 P
25	Warm spring[2]	Arkansas	June 1916	1.0	None or not more than 0.005 R
26	Deep well	Ohio	June 1916	0.1	None or not more than 0.050 R
27	Cold spring[2]	Arkansas	May 1917	2.3	None or not more than 0.016 P
28	Cold spring[2]	Arkansas	May 1917	2.3	None or not more than 0.004 P
29	Cold spring	Arkansas	Oct. 1917	2.2	None or not more than 0.002 R
30	Cold spring	Wisconsin	Nov. 1917	1.0	None or not more than 0.005 R
31	Cold spring[3]	Mississippi	Jan. 1918	1.0	None or not more than 0.009 R
32	Cold spring[3]	Arkansas	May 1920	1.0	None or not more than 0.005 R
33	Cold spring[3,4]	Mississippi	Oct. 1920	1.0	None or not more than 0.005 R
34	Deep well[3,4]	(Dup. of No. 26) Ohio	Nov. 1920	1.0	None or not more than 0.270 P
		Imported bottled waters			
35	Cold spring[2]	France	May 1914	1.0	None or not more than 0.005 R
36	Cold spring[2]	Spain	July 1914	2.4	0.079 R (0.031 P)
37	Cold spring[2]	Spain	Jan. 1915	1.0	None or not more than 0.005 P
38	Cold spring[2]	Japan	Jan. 1915	1.0	None or not more than 0.005 P
39	Cold spring[2]	Italy	Feb. 1915	1.0	None or not more than 0.005 P
40	Cold spring[2]	Norway	June 1917	0.5	None or not more than 0.010 R
41	Cold spring	Spain	Aug. 1917	0.25	None or not more than 0.020 P
42	Cold spring[2]	France	Aug. 1917	0.25	None or not more than 0.020 P
43	Cold spring[2]	Spain	Feb. 1918	0.25	None or not more than 0.020 P
44	Cold spring[4]	Austria	Jan. 1921	1.0	None or not more than 0.005 R
45	Cold spring[4]	Italy	Jan. 1921	1.0	None or not more than 0.005 R
46	Cold spring[4]	Portugal	Apr. 1921	0.19	None or not more than 0.11 R

[1] Analyst W. D. Collins. [2] Analyst F. B. Furber. [3] Analyst J. W. Sale. [4] Analyst W. E. Shaefer. [5] Either 2.0 or 2.4 liters taken.

may not be due to radium salt contained in the sample. P indicates permanent activity, due wholly to radium salt contained in the sample.

The electroscopes have a limit of sensibility corresponding to 0.005 × 10^{-9} g. of radium. It is desirable to boil out emanation from about 2 l. of water, in which case as little as 0.002 × 10^{-9} g. of radium per liter can be measured. Sometimes, however, especially in the case of foreign waters, we have available for this determination only about 200 cc., in which event the least quantity that can be measured is 0.025 × 10^{-9} g. radium per liter.

The significance of the data depends on the fact that we have never found in any commercial bottled water of natural origin sufficient radioactivity, either temporary or permanent, to warrant its purchase by consumers because of its content of radioactivity.

The largest quantity of radioactivity of a temporary nature which we have found in any commercial foreign or domestic bottled water of natural origin corresponds to 0.188 × 10^{-9} g. radium per liter. This sample came from a warm spring in Massachusetts.

The largest quantity of radioactivity of a permanent nature which we have found in any commercial foreign or domestic bottled water of natural origin corresponds to 0.270 × 10^{-9} g. (millimicrogram) radium per liter (Sample 34 in table). The activity of this sample as received was not determined. This sample came from a deep well in northern Ohio.

Let [illegible] of the two maximum figures just mentioned, 0.188 and 0.270, from a therapeutic standpoint. In "New and Nonofficial Remedies" of 1921, page 254, it is stated that the Council on Pharmacy and Chemistry of the American Medical Association will not accept any radium solution for internal use, the dosage of which is less than 2 micrograms each day, or any radium emanation generator which yields less than 2 microcuries of emanation during each 24 hrs. It is obvious, therefore, that to obtain the minimum daily dose of emanation from Sample 22 it would be necessary to consume 2810 gal. of water daily $\left(\frac{2000}{0.188 \times 3.785} = 2810.6\right)$, and to obtain the minimum daily dose of radium salt from Sample 34 it would be necessary to consume 1957 gal. of water daily $\left(\frac{2000}{0.270 \times 3.785} = 1957.0\right)$. It may be mentioned in this connection that Sample 34 is very highly mineralized, and the dose is measured by the teaspoonful.

Mellon Institute Bibliographic Series, Bulletin 1

The Mellon Institute of Industrial Research has commemorated the tenth anniversary of the use of the Industrial Fellowship System of the University of Pittsburgh by issuing Bulletin 1 entitled "A List of the Books, Bulletins, Journal Contributions, and Patents by Members of Mellon Institute of Industrial Research, 1911–1922." This is the first bulletin of the kind issued by the Institute and is the beginning of a bibliographic series which it is planned to publish. One of the provisions under which the Institute was founded is the dissemination of information concerning investigations carried out under its auspices, and this bulletin represents the published contributions of the Institute to scientific and technical literature from the inauguration of the system on March 1, 1911, to January 1, 1922.

The compilation was made by Mrs. Clara Guppy Statler, and the style is that usually followed in bibliography. In listing periodicals the abbreviations of the AMERICAN CHEMICAL SOCIETY have been followed throughout.

Studies in Rubber Vulcanization[1]

The Relation between Chemical and Physical State of Cure of Rubber Vulcanized in the Presence of Certain Organic Accelerators

By Norman A. Shepard and Stanley Krall

Research Laboratories, Firestone Tire & Rubber Co., Akron, Ohio

Hexamethylenetetramine, p-nitrosodimethylaniline, aldehyde ammonia, and the thiocarbanilide, respectively, have been introduced in such quantities in a mixing consisting of 48 parts of first latex crepe, 48 parts of zinc oxide, and 3 parts of sulfur, that equivalent physical states of cure (as gaged by the stress-strain relations) have been obtained when vulcanized for 60 min. at 287° F. (141.7° C.).

The amounts of these accelerators required to give equivalent physical states of cure were 0.5 part hexamethylenetetramine, 0.25 part of paranitrosodimethylaniline, 0.75 part aldehyde ammonia, and 1.5 parts of thiocarbanilide, respectively.

The vulcanization coefficients on these matched 60-min. cures, which were 0.87, 1.03, 0.98, and 1.38, respectively, showed no uniformity in amount of combined sulfur. In only one case, that of the p-nitrosodimethylaniline and aldehyde ammonia, did the coefficients fall closely together. In this case the difference was only about 5 per cent. In all the other cases, there was a wide variation in the coefficients; with the p-nitrosodimethylaniline the coefficient was 18.4 per cent greater, with the aldehyde ammonia 12.6 per cent greater, and with the thiocarbanilide 58.6 per cent greater than with the hexamethylenetetramine. In other words, the chemical state of cure was no index to the physical state of cure.

These four organic accelerators, though all reacting with sulfur during vulcanization, do not, when heated in xylene under similar conditions, form insoluble reaction products which seriously interfere with the determination of combined sulfur.

THE RELATIVE merits of the stress-strain relations and coefficient of vulcanization as measures of *state of cure* have been the subject of lively discussion for many years. As far back as 1902, Weber[2] stated that the fact that two different specimens of vulcanized rubber, even when produced from the same batch of crude rubber, possessed equal coefficients of vulcanization, by no means implied that the two specimens also possessed the same physical constants. It was his viewpoint that variations in the amount of working which a sample of rubber received and differences in the temperature and duration of the vulcanization period influenced the *physical result* of the vulcanization process, without exerting a corresponding influence upon the *chemical result.* Axelrod[3] has presented figures which support Weber's view that the temperature of the vulcanization largely affects the physical properties. Upon vulcanizing to the same vulcanization coefficient, but at two different temperatures, Axelrod found marked differences in the load required to produce a given elongation in the two vulcanizates. Schidrowitz,[4] in working out a systematic method for testing rubber and placing the "optimum cure" by means of "slope," came to the conclusion that the progress of vulcanization can be accurately expressed by a series of stress-strain curves, and the state of cure of a given mixing at a given time by the corresponding curve. Stevens,[5] on the other hand, while admitting that the coefficient of vulcanization can be taken only as an approximate guide to the condition or degree of vulcanization, favors this factor, rather than the physical properties, as a measure of state of cure, since the tensile properties of a vulcanized rubber are not constant, but vary with the age of the specimen, while the coefficient of vulcanization suffers little change under similar conditions; furthermore, according to Stevens, the coefficient of vulcanization is an index to the stability of the physical properties. Spence[6] takes a similar stand as regards the value of the coefficient. Eaton and Grantham[7] utilize the physical properties almost exclusively in their work on the variability of plantation rubber, though their figures[8] for combined sulfur show a very marked relationship between physical and chemical properties. De Vries,[9] though not finding such large differences as do Schidrowitz and Goldsbrough,[10] agrees with the latter that the chemical process of the combination of rubber and sulfur is in itself quite independent of the physical process which determines the position of the stress-strain curve. De Vries' arguments are based on a series of age tests conducted at 75° C. from which he concludes that it is possible to bring the rubber to the "correct" or any chosen standard of cure (as judged by the curve) with other and quite arbitrary coefficients of vulcanization. He, therefore, is of the opinion that the mechanical properties are the more important, and that the curve is a better gage for judging the properties than is the chemical condition as expressed by the coefficient of vulcanization. Stevens[11] aptly replies to this that De Vries has only shown that *under different conditions* different coefficients of vulcanization may be obtained for the same rubber, giving the same stress-strain curve. Stevens is willing to admit the value of an arbitrary "standard curve" in placing state of cure, provided the results can be correlated to rubber correctly cured in the manufacturing sense, and "it is here that the coefficient is of great value."

From this review of the literature it appears that there is considerable confusion concerning the term "state of cure." It is the opinion of the writers that to cure two samples of rubber to the same *chemical* state of cure is one thing, while to vulcanize to equivalent *physical* state of cure may be quite another. The *physical* state of cure is vital for the performance of vulcanized rubber in service, provided of course that the stability of the physical condition is certain. It is here that the *chemical* state of cure unquestionably plays a major part. It would appear, from what has already been published, that only under standardized conditions of mixing, curing, and testing is there a close relationship between the *chemical* and *physical* states of cure.

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[1] Presented before the Division of Rubber Chemistry at the 63rd Meeting of the American Chemical Society, Birmingham, Ala., April 3 to 7, 1922.

[2] "The Chemistry of India Rubber," p. 93.

[3] *Gummi-Ztg.*, **24** (1909), 352; *J. Soc. Chem. Ind.*, **29** (1910), 54.

[4] *Rubber Industry (London)*, **1914**, 212; cf. *J. Soc. Chem. Ind.*, **34** (1915) 842.

[5] *J. Soc. Chem. Ind.*, **35** (1916), 872.

[6] *India Rubber J.*, **52** (1916), 861.

[7] *J. Soc. Chem. Ind.*, **34** (1915), 989; **35** (1916), 715.

[8] *Agr. Bull. Federated Malay States*, **27** (1918), 139.

[9] *India Rubber J.*, **53** (1917), 101.

[10] *Ibid.*, **51** (1916), 505.

[11] *Ibid.*, **53** (1917), 220.

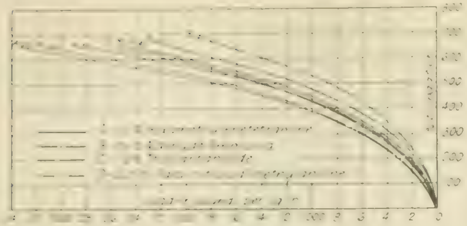

FIG. 1

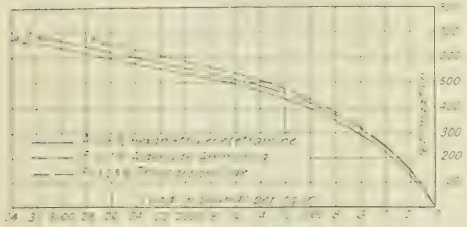

FIG. 2

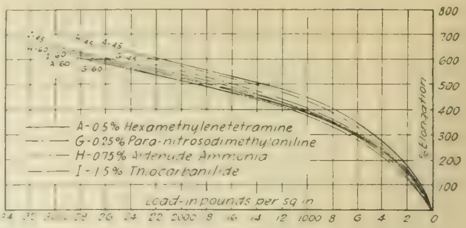

FIG. 3

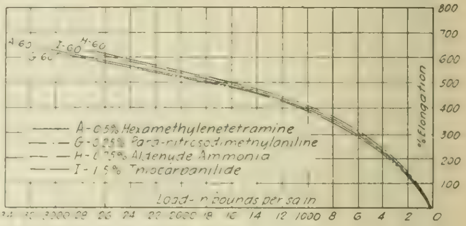

FIG. 4

With the advent of organic accelerators the relationship between the vulcanization coefficient and physical properties came to be more and more questioned. Cranor,[12] in curing smoked sheet compounded with 6 per cent of sulfur and 1 per cent zinc oxide, without accelerator and in the presence of hexamethylenetetramine and of dimethylammonium dimethyl-dithiocarbamate, respectively, found that when cured to practically the same coefficient of vulcanization (2.85, 2.83, and 2.68, respectively), the loads required to produce an elongation of 700 per cent were 700, 2070, and 2910, respectively. The periods of cure in these cases were all of different length: 130 min. at 292° F., 50 min. at 292° F., and 5 min. at 295° F., respectively. Furthermore, in spite of the moderate coefficient obtained in each case, Cranor stated that the 50-min. "hexa" cure was somewhat overvulcanized and that the 5-min. "carbamate" cure was much overcured. Similar results have been obtained when vulcanizing samples to the same coefficients with *p*-nitrosodimethylaniline.[13]

Viewing his results from the standpoint of constant physical properties, Cranor has shown that when the three stocks mentioned above were cured to the point where a load of 1000 lbs. per sq. in. was required to produce an elongation of 700 per cent, the respective coefficients were approximately 4.9 for the unaccelerated stock, 1.8 for the hexamethylenetetramine stock, and 0.9 for the stock containing the dimethylamine addition product. The coefficients of vulcanization were thus no index to the physical state of cure in [illegible]

In order to throw further light upon the relation between the chemical and physical states of cure in the case of accelerated stocks, the writers have investigated the behavior of hexamethylenetetramine, *p*-nitrosodimethylaniline, aldehyde ammonia, and thiocarbanilide, when introduced in such quantities that equivalent physical states of cure are obtained when cured for the *same* length of time at the *same* temperature. In this way each stock was subjected to identical heat conditions, which, from the above review of the work of previous investigators, appears to be of paramount importance if a fair comparison of stress-strain data and vulcanization coefficients is to be made. In matching the physical states of cure of these stocks, no attempt was made to work with the so-called "optimum cure." The cure selected was somewhat below that of maximum tensile strength (cf. the control stock A, Fig. 5) and was judged to be a good commercial cure.

EXPERIMENTAL PROCEDURE

COMPOUNDING—A selected batch of massed first latex crepe was used throughout the work and the mixing consisted of 48 parts of rubber, 48 parts of zinc oxide, and 3 parts of sulfur, to which was added the required amount of accelerator necessary to give, when cured for 60 min. at 287° F. (141.7° C.), a vulcanizate having stress-strain relations which would match those produced by using 0.5 part of hexamethylenetetramine (see Curve A-60, Fig. 1).

The selection of a formula with so high a percentage of zinc oxide (48 per cent by weight, 14 per cent by volume) may appear an unfortunate choice. The writers selected this for two reasons. In the first place, it was essential to work in the presence of zinc oxide, in order to bring out the full activity of at least two of the accelerators under consideration. In the second place, from the standpoint of comparing the results with certain actual compounds used in factory practice, it was desired to use a somewhat highly compounded stock. The writers are aware that this procedure, by flattening out the stress-strain curves and bringing those for successive cures nearer together, made the selection of identical stress-strain curves more difficult, at the same time complicating the analysis for combined sulfur.

The organic accelerators were all carefully tested for purity. The hexamethylenetetramine was the chemically pure material; the *p*-nitrosodimethylaniline melted at 83° to 84° C.;[14] the aldehyde ammonia, melting at 93° to 95° C.,[15] was so free from the resinous decomposition products with which it is commonly contaminated that it was easily ground to a

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[12] [illegible]

[13] [illegible] Delft, [illegible]

[14] Schraube gives melting point of pure material as 85° C.

[15] Melting point variously given in the literature: Beilstein, 70° to 80°; Aschan, 96° to 98° C.

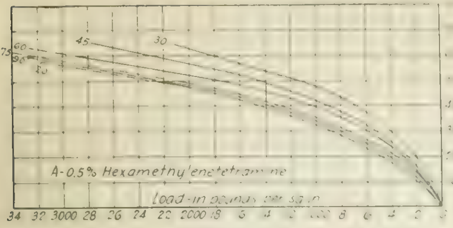

FIG. 5

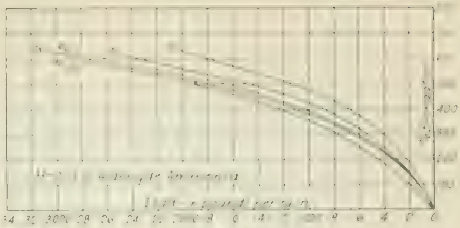

FIG. 7

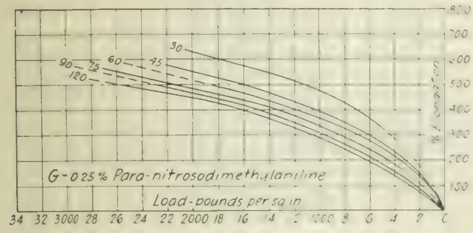

FIG. 6

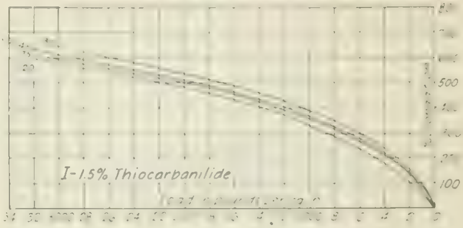

FIG. 8

fine powder; and the thiocarbanilide was twice recrystallized from alcohol and melted at 149° to 150° C.[16]

Three trial experiments were made before the amounts of these three accelerators were arrived at, which were necessary to give the same stress-strain curve in 60 min. at 287° F. as 0.5 part of hexamethylenetetramine.

The complete list of compounds investigated is given in Table I.

TABLE I

	CONTROL	EXPT. 1			EXPT. 2		EXPT. 3		
	A	B	C	D	E	F	G	H	I
First latex crepe	48	48	48	48	48	48	48	48	48
Zinc oxide	48	48	48	48	48	48	48	48	48
Sulfur	3	3	3	3	3	3	3	3	3
Hexamethylene-tetramine	0.5	..	..	..	..	..	..	..	..
Aldehyde ammonia	..	0.5	..	..	0.7	..	..	0.75	..
Thiocarbanilide	..	..	1.0	..	..	1.25	..	..	1.5
p-Nitrosodimethylaniline	..	..	..	0.22	..	..	0.25	..	..

MIXING—The stocks were mixed on a small experimental mill. After milling for 10 min. to break down the rubber, the mixture of zinc oxide, sulfur, and accelerator was incorporated during the course of 4 min. and the mixing was continued for an additional 8 min. in order to obtain a uniform product. The mill rolls were cooled to approximately the same temperature before mixing each batch and kept the same distance apart for all mixes. After mixing, the stocks passed directly to a small calender where they were calendered to a thickness of approximately 0.1 in.

CURING—The curing was conducted at 287° F. (141.7° C.) in a paraffin bath regulated to within 0.5° F. The molds were allowed to remain in a preheating bath at approximately 320° F. for exactly 1 min. before they were placed in the curing bath. This procedure was necessary to prevent reducing the temperature of the curing bath when inserting molds. After vulcanization, the molds were immediately plunged into a tank of cold water. The slabs produced were approximately 0.07 in. thick.

PHYSICAL TESTING—Dumb-bell strips were cut from the vulcanized slabs 0.25 in. wide at their central portion. The stress-strain data were obtained on the Scott testing machine by two observers. Strips of this thickness permitted the employment of the inner scale on the machine so that the load could be easily read to 0.4 lb. Two strips of each cure were broken except where otherwise stated.

ANALYTICAL METHOD—The combined-sulfur figures and vulcanization coefficients were determined in the following manner: 1-g. samples, creped on a tight cold mill, were extracted with acetone for 16 hrs. in an Underwriters extraction apparatus. After air-drying for about 15 min., the acetone-extracted samples were digested for 8 hrs. in a 5 per cent alcoholic potash solution, followed by a 16-hr. extraction with alcohol. After another air-drying, the samples were covered in a small flask with a mixture of 20 cc. ether and 20 cc. concentrated (aqueous) hydrochloric acid and allowed to stand at ordinary temperature for 1 hr. with occasional shaking. After a washing with hot water a final extraction was made with boiling water for 4 hrs. This procedure is similar to that of Kelly,[17] the ether-hydrochloric acid treatment being that proposed by Stevens.[18] The sulfur was determined in the extracted samples by the method of Waters and Tuttle,[19] by oxidizing with nitric acid-bromine mixture and fusing with potassium nitrate-sodium carbonate

TABLE II

PERCENTAGE ELONGATION	LOAD—LBS. PER SQ. IN.							
	45-Min. Cure				60-Min. Cure			
	A	B	C	D	A	B	C	D
200	235	166	213	205	324	212	[illegible]	290
300	470	302	467	465	605	392	508	610
400	825	510	790	810	1010	670	845	1025
500	1410	865	1300	1340	1720	1110	1380	1620
600	2240	1375	2080	2060	2680	1770	2120	2600
Break	(637) 2770	(675) 1840	(620) 2310	(650) 2460	(656) 3380	(640) 2180	(637) 2460	(637) ..

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[16] Lellman, 150.5° C.; Bamburger, 153° C.

[17] THIS JOURNAL, **14** (1922), 196.

[18] *India Rubber J.*, **50** (1915), 187.

[19] *Bur. Standards*, Reprint 174.

mixture. It was precipitated and weighed as barium sulfate in the usual manner.

RESULTS

The stress-strain curves obtained in the three trial experiments are shown in Figs. 1, 2, and 3, and the data given in Tables II, III, and IV. Figs. 1 and 2 show that the amounts of the three accelerators in these cases were insufficient, while Fig. 3 shows that the proportions used in Expt. 3 produce almost identical stress-strain relations when the stocks are cured for 60 min. at 287° F. (141.7° C.).

TABLE III

Percentage Elongation	A		E		F
		60-Min. Cure			
200	372		308		340
300	602		540		550
400	1005		900		850
500	1660		1520		1380
600	2620		2380		2180
Break	(662) 3300	(675)	3080	(650)	2580

In order to check up the results plotted in Fig. 3, new batches of stocks A, G, H, and I were mixed and a sufficient number of the 60-min. slabs cured so that four test strips could be cut. By averaging the four individual results, the stress-strain curves plotted in Fig. 4 (data in Table V) were obtained.

TABLE IV

Percentage Elongation	A	G	H	I	A	G	H	I
	45-Min. Cure				*60-Min. Cure*			
200	248	263	266	302	330	386	315	332
300	455	560	464	605	620	685	595	652
400	788	960	805	1030	1070	1130	1010	1070
500	1325	1535	1420	1670	1820	1870	1740	1750
600	[illegible]	2360	2170	2650	2740	2660	2590	2580
Break	(637 2480	(600) 2360	(650) 2720	(637) 3080	(606) 2840	(605) 2720	(644) ..	(625) ..

TABLE V

Percentage Elongation	A	G	H	I
		60-Min. Cure		
200	290	320	298	298
300	610	655	560	575
400	1020	1100	955	975
500	1740	1780	1610	1580
600	2760	2760	2480	2540
Break	(650) ..	(620) 3000	(630) 2940	(630) ..

The stress-strain data for these four stocks, over a range of cures from 30 to 120 min. (see Table VI), are plotted in Figs. 5, 6, 7, and 8. These are introduced in this report merely to give a more complete picture of the general characteristics of these stocks.

The combined sulfur determinations on the 60-min. cures used in Fig. 4 were run in triplicate. The results, which are given in Table VII, show that these triplicates in every case checked to within 0.03 per cent of combined sulfur.

TABLE VII

Stock	Combined Sulfur Per cent Sample 1	2	3	Av.	Coefficient of Vulcanization	Increase in Coefficient over That of A Actual	Per cent
A	0.44	0.41	0.41	0.42	0.87	..	..
G	0.50	0.51	0.49	0.50	1.03	0.16	18.4
H	0.47	0.48	0.47	0.47	0.98	0.11	12.6
I	0.66	0.65	0.66	0.66	1.38	0.51	58.6

Since it has been repeatedly observed, both in this laboratory and elsewhere,[20] that the organic accelerators used in these experiments react quite readily with sulfur at or below the temperature here employed for vulcanization, it was necessary to determine whether such reaction products are completely dissolved during the extractions with acetone, alcoholic potash, and ether-hydrochloric acid, which precede the determination of true combined sulfur. Kelly[17] believes that part of these reaction products are removed by the alcoholic potash solution and the remainder by the ether-hydrochloric acid; however, he submits no proof of this, and later qualifies the above assertion by stating that, in the case of some accelerators, it is not at all certain that the sulfur reaction products can be entirely removed in this way. In order to throw some light on this point in the case of the four accelerators under consideration, they were heated with sulfur and zinc oxide under conditions approaching as closely as possible those employed during the actual vulcanization. The same proportions of zinc oxide, sulfur, and accelerator, as employed in compounding the above stocks (A, G, H, and I), with xylene[21] (boiling point 141° C.) replacing the rubber, were heated for 60 min. at 287° F. (the time and temperature actually employed in the vulcanization). At the end of this time, the xylene was distilled off under reduced pressure

TABLE VI

Percentage Elongation	A	G	H	I	A	G	H	I
	30-Min. Cure				*75-Min. Cure*			
[illegible]		214	170		342	450	338	347
[illegible]	400	428	410	607	765	822	638	750
[illegible]	682	714	680	1040	1290	1340	1110	1210
[illegible]	[illegible]	1130	1125	1680	2135	2140	1780	1940
[illegible]	1820	1785	1800	2590	..	.	2750	3100
[illegible]	(637) 2180	(637) 2070	(637) 2050	(644) ..	(620)	(562) 2740	(625) 3100	(612) ..
	[illegible]-Min. Cure				*90-Min. Cure*			
200	[illegible]	292	270	290	418	565	321	..
[illegible]	[illegible]	[illegible]	520	695	855	950	670	..
[illegible]	[illegible]	1030	895	1160	1390	1490	1100	.
[illegible]	[illegible]	1620	1470	1860	2210	2310	1800	..
600	2290		2340		.	..	2730	..
Break	(637) [illegible]	([illegible]) 2230	(619) 2500	(631)	(600) ..	(575) ..	(612) 2880	..
	[illegible]-Min. Cure				*120-Min. Cure*			
[illegible]	[illegible]	342	[illegible]	299	487	625	430	470
300	[illegible]	730	[illegible]	684	920	1020	765	865
[illegible]	1035	1190	1000	1168	1460	1630	1210	1350
500	[illegible]	1870	1610	1860	2300	2600	1920	2160
[illegible]	[illegible]		..	2900	..	.	..	..
[illegible]	(637 [illegible]	[illegible]	(631) ..	(637)	(581) ..	(525)	(600) ..	(600) ..

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[20] Peachey, Brit. Patent 113,570 (1918); Dubosc, *India Rubber World*, **59** (1919), 248; Bedford and Scott, THIS JOURNAL, **12** (1920), 33; **13** (1921), 1034.

[21] The writers are aware that, in changing from a colloidal medium (rubber) to a noncolloidal medium (xylene), the amounts of the various reaction products obtained from any given accelerator and sulfur may be differently proportioned. It would hardly be expected, however, that the nature of the reaction products would be changed.

and the resulting mass given the same extraction treatment as the rubber stocks, *i. e.*, with acetone, alcoholic potash, and ether-hydrochloric acid. The insoluble residue at the end of this treatment was collected on a Gooch crucible, washed thoroughly with hot water, and dried at 50° C. to constant weight. A blank was also run to determine the hydrochloric acid-insoluble in the zinc oxide.

The percentages of insoluble residue, after correcting for the zinc oxide-insoluble, are given in Column 1 of Table VIII, together with the figures showing what this insoluble material would amount to in the actual vulcanizates (Column 3).

TABLE VIII

ACCELERATOR	Insoluble Residue Formed Per cent	Accelerator in Stock Per cent	Insoluble[1] in Stock Per cent	STOCK
Hexamethylenetetramine	4.3	0.5	0.02	A
p-Nitrosodimethylaniline	11.0	0.25	0.03	G
Aldehyde ammonia......	5.8	0.75	0.04	H
Thiocarbanilide.........	2.0	1.5	0.03	I

[1] Owing to the small amounts obtained in each case, the presence of sulfur was only proved qualitatively; the figures cannot, therefore, be used as correction factors for the vulcanization coefficients; but since the amounts present in each stock are so small and so nearly identical, the effect on the coefficient is almost negligible.

DISCUSSION OF RESULTS

The results for combined sulfur recorded in Table VII indicate that for accelerated stocks, even when the quantity of accelerator is so chosen that equivalent stress-strain relations are obtained in the same time of cure, the vulcanization coefficients show no corresponding uniformity. This lack of uniformity in the coefficients cannot be ascribed to sulfur retained in chemical combination by the respective accelerators, as the figures in Table VIII show. In other words, then, the vulcanization coefficient of an accelerated stock is no criterion of the physical state of cure. It is interesting in this connection to note the comments of Twiss[22] along this line:

> The chemical action of sulfur on the rubber induces the physical alterations which constitute the advantage to be gained by vulcanization, but the chemical and physical processes are not necessarily strictly proportionate and some accelerators influence one more than the other. In the presence of certain accelerators the physical or mechanical alteration is disproportionately rapid, and the tensile strength attains its maximum at a coefficient of vulcanization well below the normal value.

The coefficients recorded in Table VII are all remarkably low. Other investigators, however, have recorded similar results.[23] Kelly has given figures for a thiocarbanilide stock, having a combined sulfur content of only 0.84 and a coefficient of 0.99; the physical properties of this stock, however, are not recorded. Cranor found a stock to have satisfactory physical properties with a vulcanization coefficient of 1.09; he was working, however, with the very active dimethylammonium dimethyl-dithiocarbamate, and the curing time was only 3 min.

Looking at the results from another angle, they indicate that an accelerator has a specific action in vulcanization, aside from its influence on the chemical combination between rubber and sulfur. Many of the published figures on the properties of accelerated stocks show abnormally high tensile properties for low coefficients of vulcanization. However, in most cases, it is difficult to draw any conclusion as to any specific effect of the accelerator on the vulcanization process, since the duration of the curing period has been so variable. Many have ascribed these abnormal properties entirely to the shortening of the curing period through the influence of the accelerator. By the tabulation of Gottlob's[24] results obtained with Vulkazit,[25] Seidl[26] has shown that the shorter the time of vulcanization, the higher the tensile strength corresponding to a definite combined sulfur content. Seidl states that, parallel with the strengthening of the rubber through the taking up of sulfur, a depolymerization of the rubber takes place under the influence of the heat which exerts its harmful effect to a lesser extent, the shorter the time of heating.

Aside from a theoretical interest, the results recorded in the present paper have a practical application, since for several commercially applicable accelerators, the quantities necessary for the production of equivalent *physical* states of cure have been derived. The problem of matching the physical properties of a stock in the presence of different accelerators, but under identical temperature conditions and duration of curing period, is one often confronting the rubber technologist, for shortening of the period of cure is far from the only consideration in connection with organic accelerators. Toxicity, volatility, miscibility, effect on range of cure, influence on aging properties,[27] and tendency to produce "scorching," all have an important bearing in the selection of accelerators for specific purposes. Furthermore, where a given stock, of definite stress-strain relations, has proved through years of experience in service its applicability for a specific purpose, the introduction of a new accelerator should not disturb these stress-strain relations unless exhaustive practical tests have proved the desirability of making such a change in these factors. Hence the value, in making comparative studies of accelerators, of matching physical "state of cure" and studying the relative behavior of stocks which contain *equivalent accelerating quantities* of accelerator.

The equivalent quantities which have been determined in the course of this work indicate that 1 part of hexamethylenetetramine is equivalent in accelerating power to 1.5 parts of aldehyde ammonia, 3 parts of thiocarbanilide, and 0.5 part of *p*-nitrosodimethylaniline, respectively, *in the type of stock here tested.* It does not follow, for example, that these exact relationships will hold for a stock in which the sulfur content is sharply reduced. As Twiss[28] has remarked, "the possibility must always be borne in mind that the activity of an accelerator may possibly be influenced by the proportion of free sulfur simultaneously present." Recent publications on the mechanism of the action of organic accelerators[29] would indicate that the concentration of sulfur is an important factor in their activation. Furthermore, it must not be understood that these equivalent quantities have been worked out to the limit of accuracy. Averaged stress-strain data indicate that the errors in curing and testing run upwards to 5 per cent, while the deviations of the three 60-min. stress-strain curves from the control (the 60-min. hexamethylenetetramine curve) average 7 per cent (cf. Fig. 4 and Table V). Further refinements of the equivalent quantities, though desirable from a theoretical standpoint, have not yet been made; from the standpoint of practical application, the above results are sufficiently accurate.

In a recent article entitled "The Relative Activity of Certain Accelerators in the Vulcanization of Rubber," Endres[30] arrived at somewhat different conclusions regarding the relative equivalent accelerating quantities of some of these same accelerators. The activity of 1 per cent of hexamethylenetetramine, for example, was stated to be equivalent to that of 2.5 per cent of thiocarbanilide. It is interesting to note how he arrived at these figures. Discarding without any experimental evidence the coefficient of vulcanization as a measure of state of cure, since it "presents considerable variations," Endres uses the maximum physical properties as the criterion of correct cure, *i. e.*, the maximum tensile strength (or tensile product) at break. He states that he uses the stress-strain curves to obtain supplementary information. In the case cited above this latter was apparently overlooked, as the following figures for the equivalent cures will indicate:

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[22] *J. Soc. Chem. Ind.*, **39** (1920), 125T.

[23] Cranor, *Loc. cit.;* Whitby and Smith, paper presented before the Section of Rubber Chemistry at the 62nd Meeting of the American Chemical Society, New York, N. Y., September 6 to 10, 1921; Kelly, *Loc. cit.*

[24] *Gummi-Ztg.*, **30** (1916), 303.

[25] Probably aldehyde ammonia.

[26] *Gummi-Ztg.*, **34** (1920), 797.

[27] Ditmar, *Z. angew. Chem.*, **34**, Aufsatzteil (1921), 465; *C. A.*, **16** (1922), 174.

[28] *J. Soc. Chem. Ind.*, **39** (1920), 125T.

[29] Bedford and Sebrell, THIS JOURNAL, **13** (1921), 1034; Bruni and Romani, *India Rubber J.*, **62** (1921), 63.

[30] *Caoutchouc & Gutta-percha*, **18** (1921), 11089.

Elongation	1 Per cent Hexamethylenetetramine 50-Min. Cure at 145° C. Load in Lbs./Sq. In.	2.5 Per cent Thiocarbanilide 50-Min Cure at 145° C. Load in Lbs./Sq. In.
100	185	114
200	333	228
300	556	458
400	964	725
500	1700	1140
600	2800 (break)	1980
675	...	2660 (break)

Endres' results are further invalidated by the fact that the hexamethylenetetramine stock (above) contains 6 per cent of sulfur (to the rubber), while the thiocarbanilide stock contains 8 per cent. It is difficult to understand how a logical comparison can be drawn under such circumstances.

Quantitative Determination of Anthraquinone[1,2]

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A method has been developed by which anthraquinone may be determined quantitatively in mixtures containing also phenanthraquinone, anthracene, phenanthrene, phthalic anhydride, phthalic acid, or other oxidation products of anthracene or phenanthrene.

The method consists essentially of reducing the anthraquinone to the red oxanthranol using zinc powder and 5 per cent solution of sodium hydroxide. The red solution is filtered in vacuum and titrated with standard potassium permanganate.

A detailed outline for carrying out the analysis is given, together with several representative results showing the accuracy of the method.

IN A PAPER from the Color Laboratory by H. F. Lewis[3] a method is described by which anthraquinone may be determined quantitatively and with a fairly high degree of accuracy. While this method seems to be theoretically good, the authors have found it very troublesome because of the great length of time consumed in filtering and thoroughly washing the finely divided anthraquinone.

Grabe and Liebermann[4] found that by the reduction of anthraquinone with zinc dust and dilute sodium hydroxide, a red compound to which they gave the name of oxanthranol, or anthrahydroquinone, was formed. This compound, which is soluble in the solution of sodium hydroxide, is very readily reoxidized to anthraquinone. Since the reduction to oxanthranol and the subsequent oxidation back to anthraquinone are quantitative, these reactions formed the basis for Lewis's method of determining anthraquinone. Lewis's method as outlined consists essentially of first reducing the anthraquinone with zinc and a 5 per cent solution of sodium hydroxide to the red oxanthranol, then reoxidizing it by shaking in air and weighing the anthraquinone recovered.

As already stated, the chief difficulty encountered in this process was the filtering of the recovered anthraquinone from the alkaline solution because the finely divided precipitate invariably clogged the pores in the asbestos mat of the Gooch crucible. In several of our experiments the time required for filtering alone was nearly a day.

In the modified method this filtering is eliminated and the red solution of oxanthranol is titrated with standard potassium permanganate, thus determining the anthraquinone volumetrically instead of gravimetrically as in the older methods. But as the oxanthranol solution is readily oxidized in air, the titration with potassium permanganate must be done in a vacuum or in the presence of an indifferent gas or vapor. It was therefore necessary to design a special apparatus for this purpose. The filtering tube, a somewhat magnified diagram of the construction of which is shown in Fig. 1A, was approximately 3.5 cm. inside diameter and 24 cm. long, and drawn down to a diameter of about 5 mm. On the bottom of this tube were placed an ordinary Witte filter plate, A, ground down to fit inside the glass tube, and an asbestos mat, B, $^1/_{16}$ in. thick, which was held in place by a 100-mesh brass gauze, C. Several dents were made in the wall of the tube just above the brass gauze to keep it in place, when the stirrer was set in motion. As brass is affected very little by alkali, one gauze would last through a large number of runs. The reducing and filtering tube was made of heavy pyrex glass.

The following procedure for making an analysis has given very satisfactory results, and it can be completed in about a half hour:

Weigh out 0.5000 g. of a very finely ground sample and mix this with 3 or 4 g. of zinc dust. The finer the sample and the more thoroughly it is mixed with the zinc dust, the more readily reduction takes place. A good way is to mix the sample and the zinc dust in an agate mortar, and stir the mixture until no yellow particles or streaks of anthraquinone are visible.

From the mortar, if one is used, transfer the dry mixture to a small beaker (150 to 200 cc.). Pour in about 100 cc. of boiling 5 per cent solution of sodium hydroxide and allow the solution to stand with occasional stirring for about 5 min. The temperature of this solution should be a trifle below the boiling point of the mixture, and the heating should not be continued too long. Too long heating results in the formation of some anthranol[5] which contains one oxygen atom less than does the oxanthranol.

Run through the filter enough water that has previously been boiled and allowed to cool somewhat to form a layer about an inch deep in the bottom of the suction flask. Evacuate the suction flask until the air has been completely displaced by water vapor. The purpose of this is to sweep out all the air from the apparatus, thus obviating any oxidation of the red solution by oxygen other than that obtained from the potassium permanganate.

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[1] Received [illegible]

[2] [illegible] the [illegible]

[3] [illegible] 10 [illegible]

[4] Ann., 160 [illegible]

[5] Liebermann and Gimel, *Ber.*, **20** (1887), 1854.

Pour the red solution, together with the zinc dust and unchanged anthraquinone, into the reducing and filtering tube (Fig. 1, C), which should be kept hot by means of the electric heater D. If a rheostat is placed in the circuit the temperature of the heater can be kept very constant at about 90° to 95° C., which is about right for the best results.

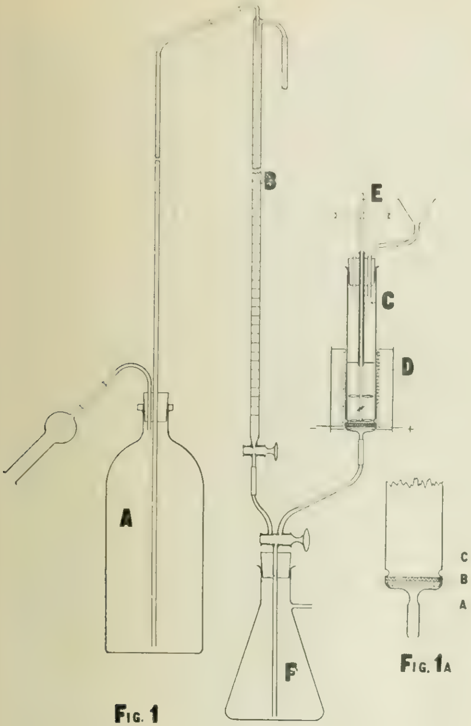

Fig. 1A

Fig. 1

A—KMnO₄ Bottle
B—Buret
C—Reducing and Filtering Tube
D—Electric Heater
E—Stirrer
F—Suction Flask

In filtering, care must be taken that no air is drawn into the filter flask. This is best accomplished by always leaving a small quantity of the solution in the filter tube. In order that the surface of the solution might be seen while filtering, the electric heater was held in place by a clamp fastened to a ring stand, and could thus be raised or lowered at will.

If care is exercised during filtration, two layers will form in the suction flask. This is highly desirable, inasmuch as the water already in the flask, which forms the upper layer, has been boiled free from dissolved air, thus protecting the red solution from any action of atmospheric oxygen.

Usually three or four reductions are sufficient, although unless the sample is very finely powdered six or eight may be necessary. The reduction must be continued until no more red solution is formed in the reducing tube after heating and stirring for about 5 min.

When the reduction has completed, fill the reducing and filtering tube approximately half full with the hot sodium hydroxide solution. After each increment of the titrating solution has been drawn into the filter flask, turn the two-way stopcock so as to admit some of this alkaline solution to wash out the potassium permanganate solution lodged in the tube between the stopcock and the solution in the flask.

The potassium permanganate used was prepared by dissolving 3.8 g. per liter and allowing the solution to stand for several days. The standardization of the solution was accomplished by grinding 0.5000 g. of pure anthraquinone to an impalpable powder and thoroughly mixing it with zinc dust. The reduction was then carried out as previously described.

The presence of phenanthraquinone with the anthraquinone does not interfere with the determination of the latter. Several runs were made in which anthraquinone and phenanthraquinone were mixed in different proportions, but in every case the results obtained were well within the limits of experimental error. It should be noted at this point that if the sample contains only pure anthraquinone, as when standardizing the potassium permanganate solution, the end-point is reached when the solution in the filter flask becomes perfectly colorless. Upon the addition of more titrating solution the color changes to a dark green, owing to the formation of potassium manganate (K_2MnO_4). If phenanthraquinone is present, the solution has a slightly bluish green tinge for the end-point, which upon addition of more potassium permanganate solution changes to a brownish green color, becoming darker. This color change probably may be explained by assuming that a derivative of phenanthraquinone analogous to oxanthranol is formed by the action of zinc and sodium hydroxide solution, and that this compound is not as readily oxidized back to phenanthraquinone as oxanthranol is to anthraquinone. From the results obtained, after having made scores of determinations of anthraquinone in mixtures containing also phenanthraquinone, anthracene, phenanthrene, phthalic anhydride, and phthalic acid, together with other oxidation products of anthracene and phenanthrene, it has been observed that there is a distinct change in color of the solution in the suction flask after sufficient titrating solution has been run in to oxidize all the oxanthranol.

Table I, showing a few results obtained on mixtures of anthraquinone and phenanthraquinone, will give an idea of the degree of accuracy obtainable with this method.

Table I

Weight of Anthraquinone Grams	Weight of Phenanthraquinone Grams	Proportion of Anthraquinone Per cent	$KMnO_4$ Solution Cc.	Anthraquinone Determined Per cent	Remarks
0.5000	0.0000	100.00	37.85	100.00	Blank Standardization
0.4750	0.0250	95.00	36.00	95.11	
0.4500	0.0500	90.00	34.00	89.83	
0.4250	0.0750	85.00	32.20	85.07	
0.4000	0.1000	80.00	30.30	80.06	
0.4000	0.1000	80.00	30.22	79.81	
0.3750	0.1250	75.00	28.32	74.82	
0.3500	0.1500	70.00	26.40	69.75	
0.2000	0.0000	100.00	29.1	100.00	Blank. Different $KMnO_4$
0 2000	0.1000	66.667	29 1	66.667	

The observed and calculated percentages of anthraquinone agree very well. Equally good agreements were readily obtained on check runs of the same sample, thus making duplicate determinations almost unnecessary.

In Lewis's method the anthraquinone was dissolved in a small quantity of alcohol. This is not permissible in the author's modification, for the reason that the alcohol would be oxidized to acetaldehyde in the titration with the potassium permanganate solution, thus causing the results to run high.

If the precautions outlined are observed in detail the average analyst should experience no difficulty in obtaining concordant results by this method which will save much time.

Application of the Direct Dyes in Coloring Paper[1]

By Walter C. Holmes

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With paper materials in general, the best results in dyeing direct dyes in sized papers are obtained when provision is made to insure maximum retention in the form of dye and the precipitation of residual color in the form of some lake other than the aluminium lake. The color should be dyed with salt, the amount of alum used in sizing reduced to a minimum, and the addition of the alum preceded by that of calcium chloride or other suitable metallic salt, which will precipitate a lake of comparatively desirable characteristics.

With ground wood furnishes, on the other hand, the best results are obtained if the absorption of the dye is prevented entirely by preceding the addition of the color by that of the metallic salt which is most suitable.

In the dyeing of mixed furnishes containing ground wood, the same principles of color application should be followed in conjunction with the customary provisions for insuring uniformity of coloring.

The methods outlined will increase the brightness of the dyeings without incurring the disadvantages attendant upon the employment of basic dyes in conjunction with direct dyes.

By means of the employment of copper sulfate in the case of numerous individual dyes and dye combinations, a considerable range of good shades of great fastness may be obtained.

THE DIRECT, or substantive, dyes are soluble sodium salts of various color acids, characterized by an affinity for cellulose which is sufficiently strong to render practical their application in coloring paper materials without the intervention of precipitating or mordanting agencies. Their employment, accordingly, is peculiarly advantageous in coloring unsized, or lightly sized, papers and such products as "mottling fiber." The same property, on the other hand, restricts their utility in certain respects, and necessitates suitable precaution in their general application.

They are further differentiated from dyes of other classes by the relative insolubility of the lake compounds which they form in beater operation and the pronounced affinity of the latter for cellulose.

As a class, they are characterized by comparatively excellent fastness to light and by tinctorial strength and brightness of shade which are only moderate. A minor disadvantage attendant upon their employment is a tendency to mottled effects. The solubility, the completeness of color retention, with the accompanying advantage of freedom from color in back-waters, and the relatively slight tendency to result in two-sided effects in the sheet, are excellent.

In addition to characteristics common to the class, individual dyes possess, in numerous instances, distinctive qualities which make them of special value for paper application. The unique and complete stability of Pontamine Yellow SX and Pontamine Yellow CH to the action of hypochlorites; and the extreme resistance of the latter to alkali, whereby it is exceptionally qualified for employment in coloring papers in which soaps are to be wrapped, may be cited by way of example.[2]

The direct dyes find only limited application in the production of very light shades in consequence of the difficulty encountered in effecting uniformity of coloring. Their employment in the minor varieties of color application on paper is also somewhat limited, although Pontamine Black EX is utilized extensively in dipping tissues, and various direct dyes, of which the yellows are the more important, are used in coating and coloring on the calender as well as in dipping. In the coloring of blotting papers and of other unsized, or lightly sized, products and that of "mottling fiber" intended for use in "granite" or mottled papers, they are used exclusively except for a minor employment of basic colors.

The principal consumption of the direct colors, however, is in the beater coloring of sized papers in all except the lightest shades. In this extensive and important field, their employment has become general in American practice, and may be expected to increase further at the expense of other classes of colors as their merits receive more complete recognition, as improvements in dyeing practice are effected, and as the demand for color permanence in paper becomes more insistent, more particularly in view of the progress which is being made in the development of direct dyes of superior qualities.

The usual practices which obtain in the beater coloring of sized papers with the direct colors are not such as will develop their maximum tinctorial power or brilliance or, in numerous instances, their maximum fastness to light. It does not appear that the fundamental importance of the role which metallic lake compounds of the dyes play in the mechanism of the color retention has been recognized. It is upon the regulation of such lake formation that effective coloring depends.

With all metallic elements except the alkalies the direct dyes form lakes which are insoluble even at beater dilutions and which manifest a remarkable affinity for cellulose. In the beater dyeing of sized papers, the formation of such lakes is unavoidable since it is impossible to effect complete absorption of the dye by the stock. Both dye and lake contribute to the total coloring effect obtained. The essential mechanism of the dyeing is that of a limited absorption of the dye itself (the soluble sodium salt of the color acid), followed by the precipitation upon the stock of such portions of the dye as remain in the liquor, in the form of the aluminium lake (the insoluble aluminium salt of the color acid), upon the addition of the alum required in the sizing. The total percentage retention of the color is very high, except when very heavy shades are run, but that factor alone is not decisive in evidencing the efficiency of the practice. The true effectiveness of the dyeing is dependent upon the degree in which the color is retained in the more advantageous form, which is, invariably, that of the dye.

When dyed in the form of dye the color is superior in both tinctorial strength and in brightness of shade, in degrees which are variable with different dyes but which are usually of a material order. With certain exceptions, into which other considerations enter, which will be noted subsequently, it is essential in obtaining optimum results, therefore, that the retention of the color should be in the form of dye, so far as may be possible, with a minimum degree of lake formation; and the effectiveness of any dyeing practice must be rated on the basis of the degree in which that condition is obtained. In ordinary trade practice, wherein no provision is made to increase the absorption of the dye, less than one-third of the color present in dyeing 6-lb. shades is generally absorbed as such and escapes precipitation in lake form.

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[1] [illegible] at the 63rd Meeting of the [illegible] April 3 to 7, 1922.

[2] [illegible] dyes, as well as those of colors of other classes, as are of essential interest to the paper manufacturer have been compiled in a chart to be included in a chapter on "The Coloring of Paper" in a vocational-educational textbook which will receive early publication by the American Pulp and Paper Association.

Quantitative data on the absorption of two representative direct dyes in 6-lb. shades with bleached sulfite and ground wood furnishes are given in Table I. The stock received a beating corresponding in duration to average beater practice before the introduction of the color.

TABLE I—PERCENTAGE COLOR RETENTION IN 6-LB. DYEINGS

TIME Min.	Temperature	Salt Lbs.	BLEACHED SULFITE	GROUND WOOD
PONTAMINE BLACK EX CONC.				
15	Room	0	30.4	25.5
30	Room	0	29.6	24.2
60	Room	0	31.5	27.0
15	140° F.	0	44.6	50.5
15	Room	40	58.8	61.3
15	Room	80	67.3	65.7
30	Room	40	56.5	61.5
30	Room	80	67.2	68.3
15	140° F.	40	64.2	68.6
PONTAMINE SKY BLUE 5BX				
15	Room	40	63.5	50.8
15	140° F.	40	50.8	38.1
30	Room	0	25.4	28.6
30	140° F.	0	.	19.0
30	Room	40	68.3	60.3
30	Room	80	70.0	60.8

The majority of dye concerns advocate the practice of dyeing their direct dyes with 40 lbs. of salt and at a temperature of 140° F.; a recommendation which is usually ignored by the paper trade unless very heavy shades are to be run. The general specification of the elevated temperature is ill advised, both by reason of the deleterious effect which its employment has upon the sizing of the paper and from consideration of coloring alone. With such dyes as are improved in retention thereby, the gain is not materially more considerable than that which may be effected with the employment of salt alone, whereas the absorption of other dyes is inhibited by heat in a decided degree.

The employment of salt, on the other hand, is not attended by unfavorable effects in general and is decidedly effective in promoting color absorption. The advantage to be derived thereby varies with individual dyes in proportion to the degree of superiority of the dye over its lake in respect to brightness and strength. With such colors as Pontamine Sky Blue 5BX, the lake of which is inferior to the dye in only a moderate degree, a 6-lb. dyeing made with 40 lbs. of salt is equivalent in strength to a 7-lb. dyeing without salt, and is decidedly brighter. With Pontamine Fast Pink BL, which is typical of dyes which are more seriously affected by conversion into their aluminium lakes, a 6-lb. dyeing with 40 lbs. of salt is fully equivalent in strength to a 9-lb. dyeing in general practice, and is brighter to an extreme degree.

The improvement in strength and brilliance cited, together with an attendant minor advantage of a more complete retention of color in heavy shades, is entirely consequent upon the limitation of lake formation which the employment of salt effects. A further improvement, which is material in degree with the majority of direct colors, may be effected by modification of the character of lake formation. The aluminium lakes of the dyes have particularly unfavorable characteristics. With the great majority of colors the calcium, barium or magnesium lakes are decidedly brighter and more attractive in shade, while even the iron lakes are often appreciably superior to those formed with alum. It is due to these facts that the presence of mineral impurities in the beater, such as may occur in the water or find introduction in the stock, is beneficial rather than otherwise in its influence on the shades obtained in dyeing sized papers with direct dyes in the usual practice. It should be noted, incidentally, that the preliminary addition of alum to the beater in order to effect the removal of such mineral impurities is, therefore, decidedly injudicious in so far as regards its influence on the shades obtainable with the direct colors.

The best results in dyeing the direct dyes in sized papers, therefore, are obtained only when provision is made which insures a maximum color retention in the form of dye and a precipitation of residual color in the form of such metallic lakes as are most suitable in the case of the individual dyes. As a general practice, it may be recommended that the calcium lakes be utilized, and that precipitation be effected by means of the addition of suitable amounts of calcium chloride. A subsequent addition of alum is essential in obtaining the best results in respect to sizing, but the amount of alum employed, which will be less than is normally necessitated, should be restricted so far as is possible. By compliance with the principles of color application outlined above, results are obtained which are, in general, greatly superior to those obtained in usual practice.

A limited number of direct dyes which find application on paper exhibit a decided susceptibility to such conditions of acidity as obtain in the paper beater in usual practice; with such it is customary to advocate the employment of limited amounts of soda ash. An excess of soda ash over the amount required to neutralize the acidity of the alum is attended by serious interference with the satisfactory sizing of the paper, and by color losses consequent upon the instability of the color lake to alkalies, but the use of restricted quantities has no more serious consequences than a possible increase in frothing. With colors of this type the improvement effected by the employment of salt and calcium chloride is of about the same order as that obtained by a resort to the use of soda ash. It is probably impossible to employ such dyes in the beater coloring of sized papers in such manner as to develop their maximum excellence of shade without entailing some measure of disadvantage in certain other respects. It is fortunate that their employment is becoming less necessary by reason of the increasing availability of dyes of similar shade and superior qualities.

GROUND WOOD FURNISHES

The general practice advocated for the direct colors is not recommended in the coloring of ground wood furnishes, wherein certain particular considerations enter. The phenomenon of color absorption in the form of dye is not one in which mere surface deposition of color is the entire, or even the predominant, component, but involves a decided degree of penetration of color within the fiber substance, whereas the dye lakes are deposited upon the fiber surface. In the particular instance of ground wood, it is found that the opacity of the stock operates to mask and obscure such portions of the dye as have become deposited within the fiber. With yellow dyes the effect observed is not pronounced, but the impairment in tinctorial strength and brightness of direct dyes, in general, is very material. In dyeing Pontamine Sky Blue 5BX, for example, in 6-lb. shades upon bleached sulfite and ground wood furnishes, it is found that the depth of shade developed on the bleached sulfite stock is several times greater than upon the ground wood, although there is no material difference in the amount of dye actually absorbed. It is possible to obtain shades of better brightness and of considerably greater depth in the case of ground wood by dyeing in the form of lake.

In the coloring of ground wood furnishes, therefore, it is advantageous, in general, to obtain color retention in the form of some suitable lake with the entire avoidance of absorption of the dye itself, as may easily be effected by the addition of a suitable amount of calcium chloride, or other metallic salt, prior to the introduction of the dye. The dyeings obtained thereby are brighter and stronger, in a degree which varies with the color and absorption characteristics of individual dyes and, in some measure, upon the amount of color employed, but which is generally considerable.

Mixed Furnishes

In the dyeing of mixed furnishes containing ground wood, wherein difficulty is encountered in effecting uniformity of coloring in consequence of the decided difference in depth of shade obtained with ground wood and with the other ingredient materials under identical dyeing conditions, the general manipulation of the customary practice should be followed. The ground wood should be introduced into the beater and receive a preliminary and partial coloring before the other stock and the remainder of the color are introduced, or the greatly preferable course of a dyeing in separate beaters with a subsequent combining of the stocks followed when the necessary equipment is available. In either case, however, the general provisions which have been outlined as essential to the effective coloring of the separate stocks should be followed. It will not be found possible to obtain complete effectiveness in coloring if it is necessary to carry out the dyeing in a single beater. The best results possible in that case are obtained by adding the ground wood, a suitable amount of mineral salt, a portion of the color, the remaining stock, the remainder of the color, salt, and a second suitable amount of mineral salt, size, and alum in the order given. The operation is not essentially more complicated than the usual practice in such cases and will give decidedly better dyeings in respect to strength and brightness. The degree of uniformity of coloring effected will be dependent, as it is in the more usual practice, upon the correct determination of the proportion of the color which is to be added at the beginning of the dyeing.

These methods which have been advocated for the application of the direct dyes are found to have an influence which is very slightly favorable, rather than otherwise, upon the stability of the dyed product to photochemical action. On the other hand, the employment of basic colors in conjunction with direct colors affords, at best, products of only moderate stability to light, and may result, under unfavorable circumstances, in products of but slight fastness, in color losses, and in variations in shade. The lake compounds of direct and basic dyes are not of superior characteristics when formed under the most favorable conditions, while compounds are formed, in other circumstances, which are undesirable in shade and inferior in brilliance, are soluble under beater conditions, and possess an affinity for cellulose which is of a low order. The brightness of the direct dyes is amply sufficient in the great majority of fields of application provided the methods by which they are applied are such as are suitable.

Copper Treatment

Although it is well known that the Sky Blues may be improved in fastness to light by a treatment with copper sulfate, it does not appear to be recognized widely that the treatment is of any decided practical value and may be extended to any considerable variety of dyes. The relative fastness of the copper lakes and the degree in which the fastness of the dye is effected by conversion into the lake, vary considerably with different dyes.

The influence of conversion into the lake upon the shade is equally variable. In general, the copper lakes are even duller than the aluminium lakes, but in numerous instances they are moderately bright and attractive in shade, while with certain direct yellows they are superior in desirability of shade to other metallic lakes of the dyes in question and but little duller than the latter. By the judicious employment of copper treatments in dyeing various individual dyes and dye combinations it is possible to obtain a great variety of shades of satisfactory brightness and excellent permanence.

The following dyes are improved in fastness in a material degree by conversion into the copper lakes:

Pontamine Sky Blue 5BX
Pontamine Sky Blue 6BX
Pontamine Blue AX
Pontamine Copper Blue 2RX
Pontamine Brown CG
Pontamine Scarlet 4BS
Pontamine Scarlet 8BS

With the exception of Pontamine Sky Blue 5BX, of which the lake is deficient in brightness, these dyes give lakes of satisfactory brightness and tinctorial power as well as of excellent fastness. The lake shade of Pontamine Blue AX is a neutral blue; that of Pontamine Sky Blue 6BX a very greenish blue, and that of Pontamine Copper Blue 2RX a very reddish blue, whereby a very extensive range of blue shades is possible.

A second list of dyes which are improved in fastness by copper sulfate in a degree which is moderate, although not sufficient to warrant the treatment in their cases, but which may be employed to advantage in shading the dyes of the first list, would include:

Pontamine Diazo Black BH Conc.
Pontamine Blue BBF
Pontamine Brown D3G
Pontamine Fast Orange S

A third list of dyes which are not improved in fastness by a copper treatment but which retain their original excellent fastness and are only very slightly impaired in brightness thereby, and are, accordingly, also suitable for shading the dyes of the first list, would include:

Pontamine Brown R
Pontamine Yellow CH
Du Pont Brilliant Paper Yellow Conc.
Pontamine Light Yellow 5GX

In the case of the last dye, the loss in brightness upon conversion into the lake is slightly greater than with the other dyes of the list but the fastness is excellent and the greenish cast of the shade thus obtained renders the dye particularly well adapted for employment with Pontamine Sky Blue 6BX in the production of fast greens.

Certain other direct dyes of excellent fastness, among which may be mentioned Pontamine Violet N, Pontamine Fast Pink BL, and Pontamine Fast Red F, give copper lakes which are of such inferior shades as to preclude the possibility of the employment of the dyes in conjunction with any copper treatment.

In the application of the copper treatment it is advisable to add the color to the beater first and to postpone the addition of the copper sulfate until after the color has been allowed to run for a short period, rather than to precede the addition of the color by that of the copper salt. The dyeings resulting from the former practice are somewhat stronger and brighter, as would be expected, and they are also distinctly faster to light. This may probably be explained upon the hypothesis that the lakes, although unquestionably materially faster than the corresponding dyes, are deposited entirely upon the fiber surface, in which position they are fully exposed to photochemical attack, whereas such portions of the color as have penetrated within the fiber substance are afforded some measure of protection from the influence of light through the absorption of active rays by the supernatant material and surface deposit of lake. With the possible exception of ground wood, it is advantageous to permit a measurable degree of absorption of dye before effecting the precipitation of the lake.

By the employment of the copper treatment with the dyes specified, it is possible to obtain a considerable range of attractive shades of excellent fastness which may hardly be duplicated by other means.

The Analysis of Beta-Naphthylamine[1]

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This paper describes the analysis of β-naphthylamine, and includes methods by which pure β-naphthylamine and its common impurities, namely, β-naphthol, β,β-dinaphthylamine, and α-naphthylamine, were prepared, and some of their physical properties determined.

Methods for the determination of β-naphthylamine in the presence of these impurities are presented, together with tables showing the results obtained on a large number of technical and specially prepared laboratory samples. Special modifications of the Kjeldahl-Gunning Method have been developed which give theoretical results when applied to β-naphthylamine.

Specifications for technical β-naphthylamine are suggested. Melting-point curves are presented for the systems β-naphthylamine–β-naphthol; β-naphthylamine–β,β-dinaphthylamine; and β-naphthylamine–α-naphthylamine.

The INCREASED use of β-naphthylamine in the manufacture of J-acid (2-amino-5-naphthol 7-sulfonic acid) and γ-acid (2-amino-8-naphthol-6-sulfonic acid) has emphasized the necessity for an accurate analytical method for its quantitative estimation in the presence of the more common impurities, namely, β-naphthol, β,β-dinaphthylamine and α-naphthylamine.

Preliminary Treatment

Purification of β-Naphthylamine—Technical β naphthylamine analyzing 98 per cent was dissolved in water as the hydrochloride, and the sulfate of the amine precipitated by the addition of sodium sulfate. The sulfate was filtered, placed in a separatory funnel, NaOH solution added, and the base extracted, as formed, with benzene. The base was precipitated from benzene as the hydrochloride with dry HCl gas, filtered, and the base prepared as before. The benzene solution was filtered, most of the solvent removed by direct distillation and the final traces by steam distillation. Distillation with steam was continued until approximately 50 per cent of the naphthylamine charged had been recovered. This was filtered, dried to constant weight over calcium chloride in vacuum, and ground to 80 mesh. The product was pure white in color, and odorless.

Melting point[2] (corrected) 110.1° to 110.2° C.
Crystallizing point (corrected) 109.66° C.
Per cent nitrogen Theory: 9.787; Found: 9.78, 9.75
(See Laboratory Sample 4, Table I.)

A second sample of β-naphthylamine was purified by repeated recrystallization from benzene. The same melting and crystallizing points were obtained as on the first sample. Liebermann and Jacobson[3] give 111° to 112° C. or 112° to 113° C. as the correct melting point of β-naphthylamine. This point, frequently quoted in reference works, is undoubtedly too high.

Preparation of β,β-Dinaphthylamine—The method of Merz and Weith[4] using zinc chloride ammonia as a condensing agent was employed. The crude dinaphthylamine was extracted with hot benzene and crystallized out on cooling. After six recrystallizations from benzene the product came out as silvery leaflets having a slight yellow color and a decided fluorescence in benzene solution.

	Theory	Found
Per cent nitrogen	5.20	5.18

Liebermann and Jacobson[3] give 170° C. and Palm[5] records 170.5° C. as the correct melting point of β,β-dinaphthylamine. The melting point of the product from the 5th and 6th crystallizations was 172.2° C. (cor.).

Purification of α-Naphthylamine—Refined α-naphthylamine having a melting point of 46.5° C. and crystallizing point 45.65° C. (Dewar bulb) was recrystallized nine times from benzene. The crystals from the 7th, 8th, and 9th crystallizations, as well as the crystals obtained by evaporation of the mother liquors from the 8th and 9th crystallizations, all showed a melting point of 49.2° to 49.3° C. (cor.). The crystallizing point of this product, taken in a Dewar bulb, was 48.5° C. (cor.).

	Theory	Found
Per cent nitrogen	9.787	9.76 9.77

The melting point recorded by Zinin,[6] of 50° C., appears to be somewhat too high.

Purification of β-Naphthol—The β-naphthol used for the melting-point curve was a technical product which was twice recrystallized from water, had a melting point of 121.2° to 121.3° C. (cor.), and crystallized at 120.8° C. (cor.). Three samples of resublimed β-naphthol from different sources had the same melting and crystallizing points as mentioned above. Liebermann and Palm[7] prepared β-naphthol from β-naphthylamine through the diazo reaction and obtained a melting point of 122° C. A repetition of their work gave a product with a corrected melting point of 120.65° C.

Direct Nitrite Titration Method

The results given in Table I, Method 1, were obtained using the same procedure as in Method 4, except that no separation of β-naphthol was made. A comparison of these results with those of Methods 2, 3, and 4 shows high analyses in proportion to the amount of β-naphthol present as an impurity. It is evident that this should be the case since, under the conditions of the analysis, nitroso-β-naphthol will also be formed. The direct titration of β-naphthylamine with 0.1 *N* sodium nitrite at 20° C. gives results higher than theory, even in the absence of β-naphthol, due apparently to the oxidation of diazo β-naphthylamine. Titration of technical samples with 0.5 *N* nitrite at 0° to 5° C. also yields results above theory, but which approach the true value more closely since oxidation is considerably checked at this temperature. In spite of these errors, many commercial laboratories and even manufacturers of β-naphthylamine still use this method with some slight modifications. The results obtained by this method are presented for comparative purposes in Table I, Method 1.

The attempt to devise a more accurate method of analysis resulted in the development of three methods, all applicable to technical materials, and each having certain advantages. The sulfonation method has the advantage of rapidity and simplicity, and is recommended where only the amine content is desired.

Determination of β-Naphthylamine

Sulfonation Method—Weigh 0.65 g. of the sample into a 50-cc. beaker, and add 20 cc. of 25 per cent oleum which has been previously cooled to 0° to 5° C. Stir with a glass rod and set the beaker in an ice bath. Stir occasionally and if necessary allow the sulfonation to come to room temperature to effect solution. Pour and wash the sulfonation into a 600-cc. beaker half filled with clean ice. Place the beaker on a tripod and bring to the boiling point. Boil gently for 15 min. to remove sulfur dioxide, and cool to 20° C. Bring the volume to 200 cc., add 15 cc. of concentrated hydrochloric acid, and titrate with 0.1 N sodium nitrite, using starch iodide as indicator. The titration proceeds rapidly to within a few tenths cc. of the end-point.

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[1] Presented before the Division of Dye Chemistry at the 63rd Meeting of the American Chemical Society, Birmingham, Ala., April 3 to 7, 1922.

[2] All melting points and crystallizing points recorded in this paper were taken with thermometers graduated in tenths of a degree and standardized by the U. S. Bureau of Standards.

[3] *Ann.*, **211** (1882), 41.

[4] *Ber.*, **14** (1881), 2343

[5] *Ber.*, **15** (1882), 614.

[6] *J. prakt. Chem.*, **27** (1883), 140.

[7] *Ann.*, **183** (1876), 268.

The end-point in the titration is reached if a distinct blue color develops 5 min. after the last addition of nitrite, when the solution is spotted against starch iodide solution on a spot plate.

1 cc. [illegible] nitrite = 2.202 per cent β naphthylamine

0.5 N sodium nitrite and a 3.5-g. sample can also be used, but in this case the temperature should be lowered to 0° to 5° C. to avoid oxidation by the higher concentration of nitrous acid.

Sulfonation at low temperature results in the sulfonation of β-naphthol to β-naphthol-1-sulfonic acid, which does not absorb nitrite. The following results obtained with mixtures of β-naphthylamine and β-naphthol offer proof of this point:

MIXTURE	PER CENT β-NAPHTHYLAMINE FOUND	THEORY
I	82.47	82.46
II	81.47	81.75

Results of the analysis of seven technical and four laboratory samples by this method are presented in Table I, Method 2.

When the β-naphthylamine content and an accurate determination of the β-naphthol present are desired, the benzene separation method should be used.

BENZENE SEPARATION METHOD

DETERMINATION OF β-NAPHTHYLAMINE—Weigh 3.5 g. of the sample onto a watch glass, brush into a 500-cc. Erlenmeyer flask, add 300 cc. of *dry* benzene and dissolve. Insert a 2-hole rubber stopper, with calcium chloride drying tube, in one hole and in the other a $^3/_{16}$-in. glass tube reaching to the bottom of the flask. Pass in HCl gas for 1 to 2 hrs., occasionally shaking the flask gently to insure thorough mixing and complete precipitation of the amine. Filter with suction through a 10-cm., double-jacketed, glass, hot-water funnel, using 2 filter papers and a platinum cone. Wash with 100 cc. of dry benzene saturated with HCl gas, and dry at 60° C. in vacuum. The precipitate adheres to the flask and necessitates drying the flask also, to obtain a complete recovery. Dissolve the hydrochloride in boiling water in a 600-cc. beaker, not allowing the volume to exceed 200 cc. Add 25 cc. of C. P. HCl, cool to 0° C., add a little ice to the solution, and titrate with 0.5 N sodium nitrite, as described under the sulfonation method.

1 cc. 0.5 N sodium nitrite = 2.046 per cent β naphthylamine

DETERMINATION OF β-NAPHTHOL—Evaporate the benzene filtrate to dryness on a steam bath, taking care to prevent the sublimation of β-naphthol when approaching dryness. Dissolve the β-naphthol with 10 cc. of 20 per cent caustic soda solution and dilute to 200 cc., heating, if necessary, to secure complete solution. Make slightly acid with HCl, add an excess of $NaHCO_3$ and couple with 0.05 N diazo [illegible]

1 cc. [illegible] = 0.20 per cent β naphthol

Results of the benzene separation are presented in Table I, Column 4.

Owing to the ease with which β-naphthylamine sublimes, together with the fact that certain naphthylamine monosulfonic acids are readily hydrolyzed back to the base, special modifications of the Kjeldahl method were required to give quantitative results. Reference is made to the work of Green and Vakil[8] for explanation of the type of sulfonation herein developed.

MODIFIED KJELDAHL-GUNNING METHOD

DETERMINATION OF TOTAL NITROGEN—Weigh 1.5 g. of the sample into a 50-cc. dry lipped beaker, add 20 cc. of 25 per cent oleum which has been previously cooled to 0° to 5° C. Stir with a glass rod, cover with a watch glass, and set the beaker in an ice bath. Stir occasionally, and, if necessary, allow the sulfonation to gradually approach room temperature to completely dissolve the larger crystals. Rinse down the sides of the beaker with 5 cc. of the oleum, cover with a watch glass, and let stand at room temperature (20° to 30° C.) for 15 hrs.

Transfer the sulfonation to an 800-cc., dry, Pyrex, Kjeldahl flask, through a long-stem, $2^1/_2$-in. funnel. Wash the beaker with three 5-cc. portions of hot concentrated H_2SO_4, rinsing the funnel while transferring.

Add 1 g. of mercury and place a plug of glass wool $^1/_2$ to $^3/_4$ in. thick midway in the neck of the flask. Wet the plug uniformly, using 5 cc. concentrated H_2SO_4. Place the flask upon the digestion rack and apply the flame. Heat below the boiling point for 10 min., then more briskly until, after about 2 hrs., a nearly colorless solution is obtained. Wash down the neck of flask and glass wool with 5 cc. of hot concentrated H_2SO_4 and continue digestion for 10 min. While holding the flask in an inclined position, carefully push the glass wool into the flask with a glass rod. Add 8 to 10 g. of dry sodium sulfate and continue boiling for 1 to 2 hrs. after the solution has become colorless. Cool and dilute with 300 cc. of distilled water, rinsing down the neck of flask. Add 1 g. of pure granulated 20- to 30-mesh zinc, 40 cc. of sodium sulfide solution (containing 100 g. of crystalline or 50 g. of fused sodium sulfide per liter), and shake. Add 160 cc. 36° Bé. caustic soda solution, pouring it carefully down the side of the flask, connect immediately with the distillation apparatus and shake. (Pyrex-Davisson distilling bulbs were used.)

Distil into 50 cc. of standard 0.25 N HCl diluted with 50 cc. water, until 250 cc. have passed over. Titrate the remaining acid with standard 0.25 N sodium hydroxide, using methyl orange or congo red as indicator. In a similar manner make a blank determination on the reagents and correct for the amount of ammonia obtained.

1 cc. of 0.25 N HCl solution = 2.385 per cent β naphthylamine

DETERMINATION OF ACID-INSOLUBLE MATTER

Weigh a 5-g. sample, dissolve in 150 cc. of boiling 1.5 per cent HCl, filter through a Gooch crucible which has been prepared with boiling water, wash with hot water, and dry at 100° C. to constant weight.

β-Naphthol, if present, will pass into the filtrate to the extent of at least 10 per cent. The insolubles include for the most part β,β-dinaphthylamine, being soluble under the conditions of the test to only 0.10 to 0.20 per cent. The β,β-dinaphthylamine can be isolated from the insoluble residue by solvent extraction, and either weighed or analyzed for nitrogen. The per cents of insolubles are given in Table I, Column 5.

DETERMINATION OF MELTING POINT

The melting points herein recorded for the pure compounds studied are at variance with those recorded in the literature. This is attributed, not so much to the greater purity of the compounds used (although great care was used in this work

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[8] *J. Chem. Soc.*, **113** (1918), 35; *C. A.*, **12** (1918), 804.

TABLE I

No.	METHOD OF ANALYSIS	Technical Samples 1	2	3	4	5	6	7	Laboratory Samples 1	2	3	4
1	Titration with 0.5 N $NaNO_2$ at 0° to 5° C., per cent	97.15	89.5	97.38	98.03	98.87	98.15	...	99.25	99.30	.....	99.82
2	Sulfonation and titration with 0.1 N $NaNO_2$ at 20° C., per cent	95.18 95.25	83.16	95.41	94.08	98.95 98.91	98.06	95.85	98.73	99.39	98.95	99.93 99.85
3	Kjeldahl-Gunning (modified) method, per cent	94.79	83.00	95.60	93.96	98.42	98.15 97.71	96.27	98.70	99.01	99.20	99.89 99.58
	Benzene separation, per cent amine	95.37	83.16	95.59	94.27	98.79	97.88	.	98.79	99.08	99.19	99.82
	Per cent naphthol	3.10	8.49	2.99	4.37	0.12	0.20	.	0.04	0.22	None	None
5	Insoluble, per cent	0.23	2.04	0.23	0.24	0.21	0.32	.	0.12	None	None	None
6	Melting point (° C.)	109.5	108.1	109.4	109.4	110.0	109.8	109.3	110.0	110.0	110.1	110.1 110.2

to obtain pure products), as to the fact that more accurately standardized and more finely graduated thermometers were available. Care was taken in making the observations to obtain a uniform temperature rise of 0.1° C. every 15 sec. during the last degree rise. The usual correction for stem exposure, which apparently was never used in the earlier work, was applied in all cases.

Capillary tubes of about 0.5-mm. internal diameter were made from glass tubing, which was previously cleaned with chromic acid solution, washed with distilled water, and dried with hot air.

For the melting-point determination, a portion of the finely ground sample was dried over sulfuric acid *in vacuo*, placed in a capillary tube, and attached to the thermometer which was immersed in a colorless oil bath in the usual manner.

The melting points, or minimum temperature of complete liquefaction, appear in Table I, Column 6.

MELTING-POINT CURVES—The pure compounds previously described were used in the preparation of the melting-point curves (Fig. 1) of the binary systems β-naphthylamine–β-naphthol, β-naphthylamine–β,β-dinaphthylamine, and β-naphthylamine–α-naphthylamine.

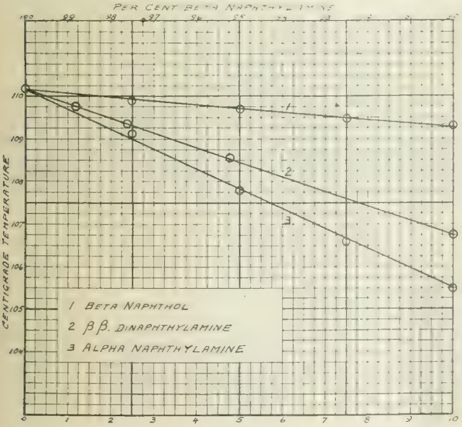

FIG. 1

The mixtures containing the desired weights of material were placed in a Parr sulfur bomb, which was tightly closed, and heated in an air oven for 15 min. at a temperature 5° to 10° above the melting point. The solid mass was removed as completely as possible, finely ground in an agate mortar, and the melting point determined.

Reference is made to the work of Kremann and Strohschneider[9] presenting the complete crystallizing-point curve for the system β-naphthylamine–β-naphthol. Their crystallizing points of 48.0° C. and 109.0° C. for α- and β-naphthylamine, respectively, are in fair agreement with those determined in this work. Their crystallizing point of 122° C. for β-naphthol is, however, undoubtedly too high.

DETERMINATION OF MOISTURE

Moisture determinations were not made on the entire series of samples because in many cases these were exhausted. However, even those which were not dried to constant weight in their preparation for analysis contained but very little moisture.

The moisture determination is made by drying a finely powdered 5-g. sample to constant weight over concentrated sulfuric acid *in vacuo*.

A sample of dry β-naphthylamine under these conditions remained constant in weight over a period of 4 days.

DISCUSSION OF METHODS AND RESULTS

In practice, the β-naphthylamine content is estimated by the sulfonation method and the melting point determined. If the amine content is 96 per cent or higher and the melting point is 109° C. or higher, the absence of any appreciable amount of impurities is assured.

If the material does not meet these specifications, the impurities are investigated further by determining the β-naphthol content by the benzene separation method and the β,β-dinaphthylamine by the solubility test.

In the benzene separation, β,β-dinaphthylamine passes into the filtrate, even to the extent of 20 per cent of the sample specified.

In the absence of appreciable amounts of β-naphthol or dinaphthylamine, the melting point of the product when compared with Fig. 1, Curve 3, offers an indication of the amount of α-naphthylamine present.

SPECIFICATIONS

In order to assist in the standardization of technical β-naphthylamine, the following specifications are suggested:

Melting point	Not less than	109.0° C. (cor.)
β-Naphthylamine	Not less than	96.0 per cent
β-Naphthol	Not more than	3.0 per cent
Insolubles	Not more than	0.5 per cent
Moisture	Not more than	0.5 per cent

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[9] *Monatsh.*, **39** (1918), 505; *C. A.*, **13** (1919), 2475.

Civil Service Examinations

The United States Civil Service Commission has announced examinations for junior engineer, junior physicist, and junior technologist, on November 22, 1922, to fill vacancies in the Bureau of Standards, Washington, D. C., or elsewhere, at $1200 to $1500 a year.

Substituted Naphthalene-sulfonic Acids[1,2]

I—A Method for Identifying H-Acid and Its Intermediates Obtained from Naphthalene-2,7-disulfonic Acid

By D. F. J. Lynch

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A method is here proposed for detecting 1,8-dinitro-3,6-naphthalenedisulfonic, 1,8 diamino-3,6-naphthalenedisulfonic, 1,8-amino-naphthol 3,6 disulfonic (H-acid), and 1,8-dihydroxy-naphthalene-3,6-disulfonic (chromotropic) acids, which occur in the nitration of naphthalene, 2,7-disulfonic acid and the subsequent reduction and hydrolysis of the dinitro acid.

THE POSSIBILITY of detecting and identifying H-acid and its intermediates by means of their insoluble organic salts was suggested by Ambler's[3] work on the naphthalenesulfonic acids. In the work here reported a large number of organic salts were prepared, but only the more insoluble ones were further studied. The method of making the salts was the same in each case. Molecular equivalent quantities of an inorganic salt of the acid and the hydrochloride of the organic base were dissolved separately in water at room temperature, the two solutions mixed, stirred thoroughly, and allowed to stand for about one-half hour. The crystallized salts were filtered, washed with cold water, and dried in the air.

All the salts were analyzed for water of crystallization in the following manner: From 2 to 3 g. of each salt, after being dried in the air, were allowed to stand in a large closed compartment until a constant weight was reached; then the salt was dried at 100° C. over sulfuric acid in a vacuum oven; the weighing bottle containing the salt was closed, put in a desiccator, allowed to cool, and weighed.

The sulfur in these salts was determined by ignition with sodium peroxide, as described by Ambler.[4]

Analysis of Salts

Benzidine Salt of 1,8 Dinitro naphthalene-3,6-disulfonic Acid ($C_{10}H_4(NO_2)_2(SO_3H)_2.NH_2C_6H_4.C_6H_4NH_2$)—This salt separates out in light yellow prisms. At 20° C., 0.036 part of this salt dissolves in 100 parts of water to give a colorless solution. It is almost equally insoluble in hot water. It contains no water of crystallization and melts with decomposition at 275° C.

Sulfur found, 11.58 per cent, 11.25 per cent
Calculated, 11.39 per cent

Cymidine 1,8 dinitro naphthalene 3,6 disulfonate ($C_{10}H_4(NO_2)_2(SO_3H)_2.[NH_2C_6H_3(CH_3)CH(CH_3)_2]_2$)—This salt separates out in straw-colored prisms. It is soluble in water at room temperature to the extent of 0.059 part in 100 parts of water. It is soluble in hot water, contains no water of crystallization, and melts with decomposition at 265° C.

Sulfur found, 9.53 per cent 9.64 per cent
Calculated, 9.47 per cent

Benzidine Salt of Chromotropic Acid ($C_{10}H_4(OH)_2(SO_3H)_2.NH_2C_6H_4C_6H_4NH_2$)—This salt separates out in brown prisms. It is soluble at room temperature in water to the extent of 0.085 part per 100 parts of water. It is nearly as insoluble in hot water, contains no water of crystallization, and melts with decomposition at 278° C.

Sulfur found, 12.89 per cent, 12.81 per cent
Calculated, 12.70 per cent

p - Nitrotoluidine - 1,8 - diamino - naphthalene - 3,6-disulfonate ($C_{10}H_4(NH_2)_2(SO_3H)_2.[NH_2C_6H_3(NO_2)CH_3]_2$)—This salt separates out in grayish tan needles. It is soluble in water at room temperature to the extent of 0.186 part per 100 parts of water. It is soluble in hot water, contains no water of crystallization, and melts with decomposition at 270° C.

Sulfur found, 10.15 per cent, 10.35 per cent
Calculated, 10.29 per cent

m-α-Naphthylamine Salt of H-Acid ($C_{10}H_4(NH_2)(OH)(SO_3H)_2.NHlC_{10}H_7$)—This salt separates out in light violet-gray prisms, is soluble in water at room temperature to the extent of 0.1006 part per 100 parts of water and nearly as insoluble in hot water, contains no water of crystallization, and melts with decomposition at 278° C.

Sulfur found, 13.67 per cent, 13.71 per cent
Calculated, 13.85 per cent

m-Pseudocumidine Salt of H-Acid ($C_{10}H_4(NH_2)(OH)(SO_3H)_2.NH_2C_6H_2(CH_3)_3$)—This salt separates out in gray prisms. It is soluble in water at room temperature to the extent of 0.097 part per 100 parts of water, is nearly as insoluble in hot water, contains no water of crystallization, and melts with decomposition at 272° C.

Sulfur found, 13.93 per cent, 13.98 per cent
Calculated, 14.10 per cent

m,p-Nitrotoluidine Salt of H-Acid ($C_{10}H_4(NH_2)(OH)(SO_3H)_2.NH_2C_6H_3(NO_2)(CH_3).H_2O$)—This salt separates out in gray prisms. It is soluble in water at room temperature to the extent of 0.106 part per 100 parts of water, is soluble in hot water, contains 1 molecule of water of crystallization, and melts with decomposition at 265° C.

Sulfur found, 13.40 per cent, 13.51 per cent
Calculated, 13.59 per cent
Water found, 3.62 per cent, 3.58 per cent
Calculated, 3.68 per cent

Tolidine Salt of H-Acid ($C_{10}H_4(NH_2)(OH)(SO_3H)_2.NH_2C_6H_3(CH_3)(C_6H_3)NH_2.3H_2O$)—This salt separates out in gray-violet prisms. It is soluble in water at room temperature to the extent of 0.102 part per 100 parts of water, is nearly as insoluble in hot water, contains 3 molecules of water of crystallization, and melts with decomposition at 260° C.

Sulfur found, 11.95 per cent, 11.87 per cent
Calculated, 12.05 per cent
Water found, 9.17 per cent, 9.12 per cent
Calculated, 9.23 per cent

Zinc Salt of 1,8-Diamino-3,6-disulfonic Acid ($C_{10}H_4(NH_2)_2S_2O_6Zn.3H_2O$)—Upon standing for about one-half hour this salt separates out in gray microscopic needles. It is soluble in hot water and contains 3 molecules of water of crystallization. The zinc was determined according to the method of Huppert and Van Ritter.[5] A weighed amount of dried salt was placed in a porcelain crucible over which was poured cold concentrated nitric acid. The whole was carefully heated until a dry residue remained, then ignited until the residue while hot was pure white. This salt dissolves to the extent of 6.4 parts per 100 parts of water at 20° C. The excess of zinc sulfate reagent has a salting-out effect.

Zinc found, 17.25 per cent, 17.18 per cent
Calculated, 17.06 per cent
Water found, 12.40 per cent, 12.49 per cent
Calculated, 12.47 per cent

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[1] Received December 3, 1921

[2] Contribution No. 57 from the Color Laboratory, U. S. Bureau of Chemistry, Washington, D. C. Published with permission of the Department of Agriculture.

[3] "Naphthalene-sulfonic Acids. II. A Method for the Qualitative Detection of Some of the Naphthalene Sulfonic Acids," by J. A. Ambler and E. T. Wherry, This Journal, 12 (1920), 1085.

[4] This Journal, 12 (1920), 1081.

[5] *Z. anal. Chem.*, **35** (1896), 311.

Identification of H-Acid and Intermediates

(Tests are to be made in 5 to 10 per cent hydrochloric acid solutions, except those with cobalt chloride and zinc sulfate, which are made in neutral solutions)

	Benzidine-HCl	2-Cymidine-H_2SO_4 ($CH_3 = 1$)	α-Naphthylamine-HCl	Pseudocumidine-HCl	Tolidine-HCl	*p*-Nitrotoluidine HCl (1-2-4)	$CoCl_2$	$ZnSO_4$
1,8 - Di - NO_2-3,6-disulfonic acid of naphthalene	Immediate ppt. Light straw-yellow. Wait 5 min.	Immediate light straw-yellow ppt. Wait 10 min.	No ppt.	No ppt.	No ppt.	No ppt.	No ppt.	No ppt.
1,8 - Di - NH_2-3,6-disulfonic acid of naphthalene	No ppt.	No ppt.	No ppt.	No ppt.	No ppt.	Gray-tan ppt. Let stand 15 min.	Brown ppt. Let stand 1/2 hr.	Ppt. brown. Let stand 1/2 hr.
1 - NH_2 - 8-OH - 3,6 - disulfonic acid of naphthalene (H-acid)	A ppt. is formed on long standing from a conc. solution	No ppt.	Ppt. light violet - gray. Let stand 15 min.	Ppt. tan-gray. Let stand 10 min.	Ppt. gray-violet. Let stand 10 min.	Ppt. gray. Let stand 10 min.	No ppt.	No ppt
1,8 - Di - OH-3,6-disulfonic acid of naphthalene (chromotrope acid)	Immediate brown ppt. Wait 10 min.	No ppt.	No ppt.	No ppt.	No ppt.	No ppt.	No ppt.	No ppt.

Cobalt Salt of 1,8-Diamino-3,6-disulfonic Acid ($C_{10}H_4(NH_2)_2S_2O_6Co.2H_2O$)—Upon standing for one-half hour this salt separates out in brown microscopic needles. It is soluble in hot water and contains 2 molecules of water of crystallization. The cobalt was determined by heating the cobalt salt slowly and carefully and then igniting the residue of cobalt oxide. This salt dissolves at 20° C. to the extent of 6 parts per 100 parts of water. Here again the excess of the molar solution of cobalt chloride has a salting-out effect on the salt.

Cobalt found,	15.31 per cent, 15.37 per cent
Calculated,	15.51 per cent
Water found,	8.71 per cent, 8.68 per cent
Calculated,	8.80 per cent

Method of Identification

All the tests may be made in test tubes with 3 to 5 cc. of dilute solutions—for example, of concentration less than tenth molar. The organic reagents should be prepared upon the same day as needed by dissolving the organic base in a 10 per cent solution of hydrochloric acid. The zinc and cobalt reagents used are molar solutions of the salts of these metals. Before making any of the following tests, however, all sulfates should be removed with barium chloride in the following manner: Bring the solution to boiling and then add an excess of barium chloride solution; allow the solution to stand on the water bath until the precipitate has settled, then filter and wash; bring the filtrate to boiling and add sodium carbonate solution to remove the barium. Neutralize the filtrate with hydrochloric acid. Of the four acids studied only two, H- and chromotrope acids, form barium salts insoluble in the cold. Both of these salts are soluble in hot water. On cooling, therefore, a precipitate indicates H- or chromotrope acid.

1,8-Diamino-3,6-disulfonic Acid—First test for 1,8-diamino-3,6-disulfonic acid, as identification of this acid should be made in a neutral solution, by adding a molar solution of cobalt chloride or zinc sulfate. After standing for one-half hour, the formation of a precipitate indicates the presence of this acid. The precipitate is compact and slow in forming. The presence of the other three acids, however, does not interfere with this precipitation. If, later on, no H-acid is found, 1,8-diamino-3,6-disulfonic acid can be quickly identified and confirmed with the reagent *p*-nitrotoluidine (1,2,4) hydrochloride. This reagent gives an immediate grayish tan precipitate with the diamino acid.

The tests for the other three acids are made in acid solution. Add enough hydrochloric acid to make the resulting mixture a 5 per cent acid solution and let stand one-half hour. If the solution so treated is a concentrated solution of H-acid, its acid sodium salt will be precipitated. Filter out this acid salt. The amount of H-acid left in solution can be easily detected with any of the reagents given in the table and the resulting dilute solution of H-acid will not interfere with the tests for the other acids.

1,8-Dinitro-3,6-disulfonic Acid—As seen from the table, cymidine hydrochloride will precipitate only this acid from any mixture of acids of this group. This test should be made before the removal of H-acid, when such removal is necessary, as this acid, like many other nitro compounds, decomposes upon heating. If, however, no chromotrope or H-acid is found afterwards, benzidine hydrochloride will serve as a reagent in confirming the presence of the dinitro acid. There is no difficulty in distinguishing the benzidine salt of the dinitro acid from the one formed with chromotropic acid. These two acids almost never occur in the same working mixture. With such a mixture, however, all the dinitro acid should be removed with a large excess of cymidine hydrochloride. Filter out the dinitro salt and neutralize the filtrate with sodium hydroxide. Filter the free base and evaporate the filtrate down to the original volume before testing for chromotropic acid.

1,8-Aminonaphthol-3,6-disulfonic Acid (H-Acid)—This acid is identified by the formation of an insoluble salt with α-naphthylamine, tolidine or pseudocumidine hydrochloride in a 5 to 10 per cent acid solution. These reagents do not form insoluble salts with the other three acids. *p*-Nitrotoluidine hydrochloride also forms an insoluble salt with H-acid in an acid solution, which will serve for identifying the acid if no diamino acid is present.

Definite positive tests have been obtained in the Color Laboratory with 2 cc. of 0.01 *M* solution of H-acid upon the addition of 2 cc. of 0.1 *M* solution of tolidine hydrochloride or *p*-nitrotoluidine hydrochloride. The results of these tests show that by this method it is possible to detect as small amounts as 0.3 per cent of H-acid in a 5 per cent solution of hydrochloric acid. *p*-Nitro-*o*-toluidine hydrochloride and pseudocumidine hydrochloride are better reagents because the salts formed are flocculent. In dilute solution the precipitates form more slowly and at least one-half hour should be allowed for the tests.

Before testing for chromotropic acid remove the H-acid present in the following manner: Add an excess of *p*-nitrotoluidine reagent and allow solution to stand one-half hour for complete precipitation. Filter, and neutralize with sodium hydroxide solution. Filter out the free base and evaporate the solution to its original volume. The solution can then be tested for chromotropic acid.

1,8-Dihydroxy-3,6-disulfonic Acid—If H-acid was present and removed with *p*-nitrotoluidine hydrochloride, test again with that reagent to make sure of the complete removal of H-acid, after which identify chromotropic acid with benzidine hydrochloride.

Experiments with Florida clay deposits, made possible by the coöperation of various Florida cities, are now being conducted at Cornell University to determine whether these clays can be used for the manufacture of brick, tile, and pottery. Clays suitable for filler are also being tested.

Coke Residue Test for Creosote Oils[1]

By **Charles S. Reeve** and **Frank W. Yeager**

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DURING the past year the authors' attention was called to rather marked discrepancies in the results of this test,[2] not only in different laboratories but with the same operator when testing oils especially prepared and distributed for comparative work.

The possible variations in the test were first shown by experiments on two samples of oils distributed to four laboratories with instructions to follow the method outlined. The results of these experiments are given in Table I.

TABLE I

	Sample 1				Sample 2			
Test	A	B	C	D	A	B	C	D
1	8.0	10.8	9.2	11.8	4.2	7.6	6.3	7.3
2	7.3	11.1	10.5	12.3	4.0	7.2	6.1	7.8
3	8.00	7.8	10.3	10.1	4.1	6.8	6.4	7.3
4	8.0	9.2	9.9	9.9	4.4	...	5.8	7.3
5		.	9.9	...	4.2	...	5.2	...
6	...	.	.	...	4.4	...	...	...
Av.	7.8	9.7	10.0	11.0	4.2	7.2	6.0	7.4

These results show a remarkable dissimilarity between the different laboratories on the same oils, and a general failure to get close checks even in the same laboratory. The variations of the tests in the individual laboratories expressed as maximum per cent variation from the average are:

LABORATORY	Sample 1 Per cent	Sample 2 Per cent
A	9	5
B	20	6
C	8	13
D	12	5

The variation between laboratories on the same oil is 19 per cent for Sample 1, and 32 per cent for Sample 2. Inasmuch as this test is used as a basis for estimating the amount of refined tar blended in a finished creosote, and as the oils are often required to fall within a specified limit in this respect, it is readily seen from these results that the test is not satisfactory.

This wide variation in results led to a consideration of the factors that might be responsible. Our conclusions may be summarized as follows:

(1) SHAPE OF BULB—While the specifications for a bulb are narrow as to shape and dimensions, we have found it practically impossible to obtain the desired uniformity, and it is usually necessary to select from a large lot those which most closely approximate the specification.

(2) CHARACTER OF GLASS—Many of the bulbs on the market are made of a soft glass, which either prevents the proper application of the full flame heat, or through fusion and consequent shrinkage of the glass walls causes a change in the relation of volume of oil to bulb capacity.

(3) RATE OF DISTILLATION—It is difficult to keep this constant on account of the small vapor space above the oil and because of the frequent necessity of conducting the distillation intermittently in order to avoid spurting, particularly when the oil contains traces of water.

Efforts were made to minimize these effects by purchasing a few special hard-glass bulbs that came very near the specifications, but in no case was there any material increase in the ability to obtain better check results. These results are included in Table II. This investigation led to the conclusion that some method should be devised that would eliminate coking in glass, but at the same time give results more nearly constant and substantially in accord with those heretofore obtained in the bulb, and so avoid as far as possible any conflict with existing oil specifications. This involved a distillation with subsequent coking of the residue and it was decided to associate the coke test with the retort distillation as given in American Society Testing Materials D-38-18.

The following procedure was therefore devised: (1) The oil was subjected to retort distillation; (2) the residue above 355° C. was subjected to the test for fixed carbon (A. S. T. M. D-22-16) using a Bunsen burner; (3) the percentage of fixed carbon (coke) was calculated back to the original sample of oil. In trying out the method, each of four oil samples was tested by two operators. Table III gives the distillation tests, percentage of coke on residue, and calculated percentage of coke on the oil.

TABLE II—SUMMARY OF TESTS COMPARING COKE BULB AND RESIDUE CRUCIBLE TESTS OF CREOSOTE OIL COKE

[illegible]	3				4				5[1]				6[2]			
Operator	1		2		1		2		1		2		1		2	
[illegible], per cent vari- [illegible]			9.1		.		5.7		3.2		3.7		0.9		..	
			±10		.		±10		±10.		±10.		±27.		..	
[illegible] distillation, per cent distillate:																
0–170° C.	0.0		0.0		0.0		0.0		0.1		0.0		0.0		0.0	
[illegible]	3.3		3.0		3.2		4.7		0.4		0.2		0.5		0.4	
[illegible]	27.6		26.2		32.2		34.6		4.6		2.4		1.8		2.3	
[illegible]	48.0		48.6		56.0		57.3		22.0		20.1		15.3		16.4	
[illegible]	[illegible]		60.1		68.2		69.4		42.5		42.3		42.0		40.9	
[illegible]	70.3		70.5		78.6		79.5		70.7		69.1		73.6		73.9	
Residue	29.0		28.9		20.2		20.4		28.7		30.7		25.3		25.7	
[illegible]	0.7		0.6		1.2		0.1		0.6		0.2		1.1		0.4	
	I	II	I	II	I	II	I	II	I	II	I	II	I	II	I	II
[illegible]	[illegible]	8.1	27.8	8.0	25.9	5.2	25.0	5.1	9.4	2.7	9.2	2.8	2.7	0.7	2.9	0.7
	[illegible]	8.0	27.8	8.0	25.9	5.2	25.3	5.2	9.2	2.7	9.2	2.8	2.7	0.7	2.5	0.6
	[illegible]	8.1	28.0	8.1	25.8	5.2	25.3	5.2	..	..	9.2	2.8	..	..	2.1	0.5
	[illegible]	8.1			25.8	5.2	.	.	..	.	..	..	..	..	..	..
[illegible]		8.1		8.0		5.2		5.2		2.7		2.8		0.7		0.6
[illegible]		±1		±1		[illegible]		±2.		0.		0.		0.		±17.
[illegible]		[illegible]		(a)		[illegible]		(a)		(b)		(a)		(b)		(a)
[illegible] bulb test		[illegible] to 10.2				5.4 to 6.3				2.9 to 3.6				0.7 to 1.0		
[illegible] bulbs						5.0–6.2 Av. 5.6										

I Per cent fixed carbon [illegible]
II Per cent coke [illegible] whole [illegible]

[1] Refined tar solution
[2] Distillate oil

a—10 cc. capsule type of crucible.
b—20 cc. regular form of crucible.

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[1] Received [illegible] 1922.

[2] Am. Soc. Testing Materials, Standard D-38-18.

Table III

(Coke Test: 355° C. Residue: 20 cc. Platinum Crucible)

	Sample 3		Sample 4	
Operator	1	2	1	2
Per cent coke	8.1	7.9	5.2	5.2
Average	8.0		5.2	

In the residue-crucible test the variation in the results of the same operator, or between two operators, is practically negligible. Furthermore, the results of the tests are comparable with the average of the regular coke-bulb test.

A few other trials were made on Oil Samples 3 and 4 using the regular type 20-cc. in place of the 10-cc. capsule crucible. These results are practically the same as those obtained by the 10-cc. platinum crucible (Table II).

To determine the possibility of further simplifying the test, some coke determinations using the crucible method and charging the oils direct to the crucibles without previous distillation, were made.

Table IV

(Per cent Coke: Oil Charged Direct to Crucible)

	Sample 3		Sample 4	
Crucible	10 cc.	20 cc.	10 cc.	20 cc.
Per cent coke	6.20	7.03	3.06	4.70
Per cent coke	6.38	6.31	3.28	4.66
Average	6.3	6.7	3.2	4.7
Range of per cent coke by bulb test	8.5 to 10.2		5.4 to 6.3	

This last procedure was not considered satisfactory with either crucible, mainly on account of the failure of the results to approximate a regular bulb test.

Reference to the tabulation will show that residue-crucible results are always slightly lower than the average coke-bulb results.

Oil sample...........	3	4	5	6
Per cent coke (bulb method)............	9.6	5.7	3.2	0.9
Per cent coke (residue-crucible method)....	8.1	5.2	2.8	0.7
Range of bulb tests....	8.5 to 10.2	5.4 to 6.3	2.9 to 3.6	0.65 to 1.0

This condition may be due to the softness of the glass bulbs which, as previously noted, makes it impossible to apply the full flame heat for period adequate for igniting the residue. Such limiting of ignition results in leaving a residue that is not entirely coked and consequently of greater per cent than an equivalent completely coked residue. Under such conditions the degree of coking may in some instances be carried further than in others, and these tests would represent purer coke residues, which, other things being equal, are indicated by the lowest per cent of coke. It is apparent on comparing the lowest bulb results with the residue-crucible averages that this assumption is approximately correct. This is also evidenced by the tests on Sample 4 using the special very hard glass bulbs, where the coke obtained by the residue-crucible method falls within the limits of the bulb variations,—*i. e.*, the range of bulb test is 5.0 to 6.2 per cent, and the average of residue-crucible tests is 5.2 per cent.

Table V—Comparison of Bulb and Crucible Tests by Different Laboratories

Oil sample	7			8			9		
Laboratory	A		B	A		B	A		B
Operator	1	2	3	1	2	3	1	2	3
Per cent coke by bulb	8.9	8.2	8.2	5.1	4.7	5.4	6.5	5.9	7.1
Variation	..	±6.	..	..	±8.	..	..	±9.	..
Average of bulb test	..	8.4	..	..	5.0	..	..	6.5	..
By residue-crucible	7.7	8.0	8.1	4.4	4.2	4.6	5.3	5.4	5.3
Variation	..	±2.5	..	..	±4.6	..	..	±1.9	..
Average residue-crucible tests	..	7.9	..	..	4.4	..	..	5.3	..
Difference between methods	..	0.5	..	..	0.6	..	..	1.2	..
Sp. gr. of oil	..	1.093	..	..	1.087	..	..	1.118	..
Per cent residue to 355° C.	..	28.3	..	..	22.5	..	..	39.4	..

Thus it appears that the residue-crucible method, while yielding results somewhat lower than the usual bulb tests, indicates more truly the actual coke content of the oil, and that as the hardness of the bulbs is increased the results by the two methods become more nearly equivalent.

A recent trial of the crucible method on three oils by different laboratories gave the results in Table V.

Conclusions

It has been found that the percentage of coke in an oil as determined by the coke-bulb test is subject to variations over undesirably wide limits, owing to unavoidable variations in test conditions, and that a crucible test wherein the percentage of coke is calculated from a fixed carbon test on the residue of the oil remaining after a retort distillation to 355° C. has the following points to recommend it as a substitute for the bulb test:

1—The results are sufficiently close to the average of a number of regular coke tests to offer comparable values.

2—The accuracy of the method is greater than that of the present coke-bulb test.

3—The procedure itself is very simple, and requires no apparatus that is not usually found in laboratories where general tar and oil tests are made.

4—The difficulty and expense of obtaining truly satisfactory coke bulbs are eliminated.

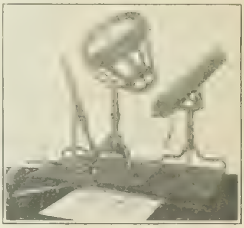
5—The oils are usually given retort distillation tests and the residue can be used for the coke test. The total time per test in such cases is, therefore, only about 15 min.

Priestley Apparatus at Dickinson College, Carlisle, Pa.

Dickinson College has for over a century treasured some fine pieces of apparatus once owned by Joseph Priestley. They were purchased for the sum of $530 by Thomas Cooper, who in 1811-1815 was professor of chemistry and mineralogy at Dickinson.

The burning glass is composed of two lenses, 16 and 7 in. in diameter, and set 16 in. apart. The wooden frame permits adjustment to suit the altitude of the sun.

The reflecting telescope is of the Gregorian type. The main mirror is 5 in. in diameter, and is mounted in a brass tube 2.5 ft. long. The maker was W. S. Jones, London.



The achromatic refracting telescope is 4 ft. long. It was made by Dolland.

The air gun was probably designed by Priestley himself. The air magazine is a wrought iron globe, 3.5 in. in diameter.

There are also flasks with ground necks and tubes with ground stoppers.

Another Platinum Theft

The following platinum articles were stolen from Vanderbilt University, Nashville, Tenn., between August 1 and 8, 1922:

	Approx. Weight Grams
Crucibles	
No. 3, with lid	19.1
No. 9, with lid	28
No. 14, with lid	39.8
No. 30, with lid	22.8
No. 34, with lid	27.5
No. 44, without lid	4.6
Milk Dish	
No. 9, gold	16.1
Combustion Boats	
No. 4, No. 5	7.1, 15.2
Dishes	
No. 20, No. 21	40.3, 31.2
Platinum combustion tube, complete, unused (E. & A. No. 5402)	377

The university will greatly appreciate any information leading to the recovery of any of these articles.

The Technical Chemistry of Vanadium[1]

By B. D. Saklatwalla[2]

Vanadium Corporation of America, Bridgeville, Pennsylvania

THE ELEMENT vanadium was discovered about a hundred and twenty years ago in 1801 in the lead ores of Mexico by Manuel del Rio. Thirty years later Berzelius had studied and worked out the chemistry of this element. By the year 1870 Roscoe had supplemented Berzelius's work and practically exhausted the study from a chemical standpoint.

In spite of this early work, vanadium had not entered the sphere of commercial technology until within the last very few years. In the sixties there was some demand for vanadium in the dyeing industry, in the preparation of aniline black. It was also used in the manufacture of inks, and for coloring glass and pottery, brown, purple, blue, and green glazes being prepared with it. Its salts had also been suggested as photographic developers, and as catalyzers in the contact process of sulfuric acid manufacture. Also its compounds had been tried as therapeutic agents owing to their strong oxygenating properties, and they had also been recommended as antiseptics. Further, their use was tried in the laboratory, as a reagent for alkaloids and hydrogen peroxide, and for the determination of hydrazine and hydroxylamine in the presence of ammonia.

The technical use of vanadium on a commercial scale, however, began when it entered the metallurgical field. In 1894 Moissan experimented on the reduction of vanadium in the electric furnace. In 1896 the Firminy Steel Works in France experimented with its use in armor plates. In 1900, however, Professor Arnold in Sheffield, England, undertook a comprehensive study of its effects in steel, and that date may be considered as its real entry into the commercial metallurgical field.

The reason for a century-long neglect of this element is to be found mainly in the fact that until comparatively recently no commercially workable deposits of vanadium minerals were known. The vanadium was extracted from slags, ashes of vanadium-bearing coals, and the like. The processes employed were long and wasteful, and consequently the cost of the vanadium was prohibitively high. Fortunately about the time its usefulness was proved in steel metallurgy by Professor Arnold, the largest known deposits of vanadium in the Peruvian Andes were discovered, consisting of the mineral patronite, a vanadium sulfide. Subsequently, in this country, deposits of vanadiferous sandstone and carnotite have been worked. The vanadiferous sandstone contains as one of its constituents "Roscoelite," a vanadiferous mica. The carnotite carries its vanadium in combination with uranium. With the discovery of these deposits the metallurgical application of vanadium advanced rapidly.

Chemical Reactivity of Vanadium

From the chemists' standpoint the element vanadium presents very interesting features which can scarcely be found in any other element. It possesses a reaction capability enabling it to form an extensive number of different compounds. We

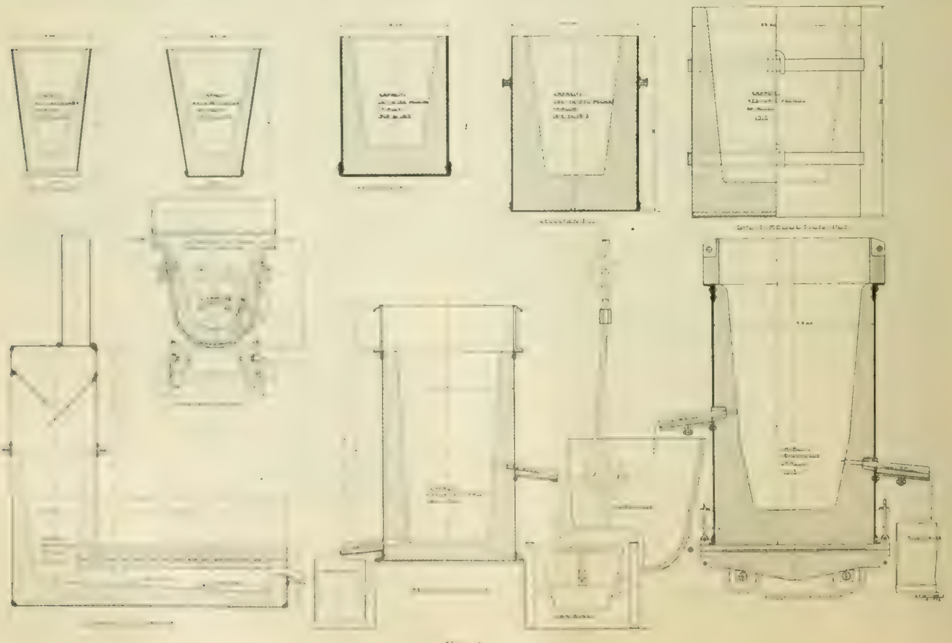


Fig. 1

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[1] Presented before the New York Section of the American Chemical Society, New York, N. Y., June 9, 1922.

[2] General Superintendent, Vanadium Corporation of America.

can readily understand this capability when we consider its position in the periodic system. It stands in the fifth group of elements vertically with N, P, As, Sb, and Bi, between P and As, and horizontally its atomic weight places it between Ti and Cr. Consequently, it shares the property of this group of functioning in different valencies and forming basic as well as acid radicals. Combined with this, its proximity to chromium imparts to it the capability of forming double salts.

The element vanadium occurs in its compounds in the di-, tri-, tetra-, penta-, and hexavalent states. The salts corresponding to the lowest oxide, VO or V_2O_2, are powerful reducing agents, capable of bleaching organic coloring matter and reducing copper, tin, silver, gold, platinum, and mercury to the metallic state from their salts. The chloride and sulfate are the best-known compounds corresponding to this valency. The sulfate is isomorphous with ferrous and chromous sulfates.

The compounds corresponding to the trivalent oxide, V_2O_3, show characteristic similarity to trivalent iron and chromium salts. With this valency also an increased tendency to form double salts is manifested. The halogen salts and sulfate with a large number of double salts, regular alums, are common. Oxalates, double oxalates, and salts of complex acids also occur.

With the next increasing step of valency, corresponding to the oxide VO_2 or V_2O_4, the number of salts increases to a very great extent. This tetravalent vanadium appears to be the most stable base, as it forms salts with almost every inorganic and very many of the organic acids. Also the tendency to form double salts with organic as well as inorganic bases is appreciable. With this state of valency the acid character of the element begins to appear with the formation of vanadites, which are extremely readily oxidized to vanadates.

With the pentavalent stage of valency the number of compounds formed, as well as tendency to form double salts, further increases. Also pentavalent vanadium very decidedly shows its acid character, with little tendency to form basic radicals. Its salts as a base with acids are comparatively few. The oxide V_2O_5 plays an important part in the technical chemistry of vanadium, as it has been the starting material for the manufacture of almost all vanadium compounds. It can be prepared in a perfectly pure state by calcination of ammonium vanadate. Obtained in this way it consists of extremely beautiful yellow-red crystals about 3 to 4 cm. long and 2 to 3 mm. wide, which readily melt at about 655° to 660° C. This oxide is the anhydride of three different acids, ortho-, meta-, and pyrovanadic acids, corresponding to the phosphoric acids. The number of vanadates formed from these three acids with inorganic and organic bases is overwhelmingly large.

Hexavalent vanadium is known to exist in the form of pervanadic acid, HVO_4, and its corresponding salts, which are little known.

This cursory knowledge of the activity of vanadium in forming large numbers of compounds with widely different properties and acting as a base or acid with change of valency, or even with the same valency, will help us to realize some of the difficulties in the technical operation of processes for extraction of the metal from the ores and of the large losses in recovery suffered in the earlier days of the industry. The realization of this fact was necessary, for instance, in the selection of a leaching agent for a particular mineral, which may have its vanadium content in a certain valency stage, or in the bringing of such vanadium content by pre-roasting, etc., to the valency state suitable to the leaching medium used, or in the selection of a precipitating agent, keeping the solution during precipitation in the right valency condition, or in selecting the right fluxes and refractory lining during the reduction of a certain valency vanadium compound to the metallic state.

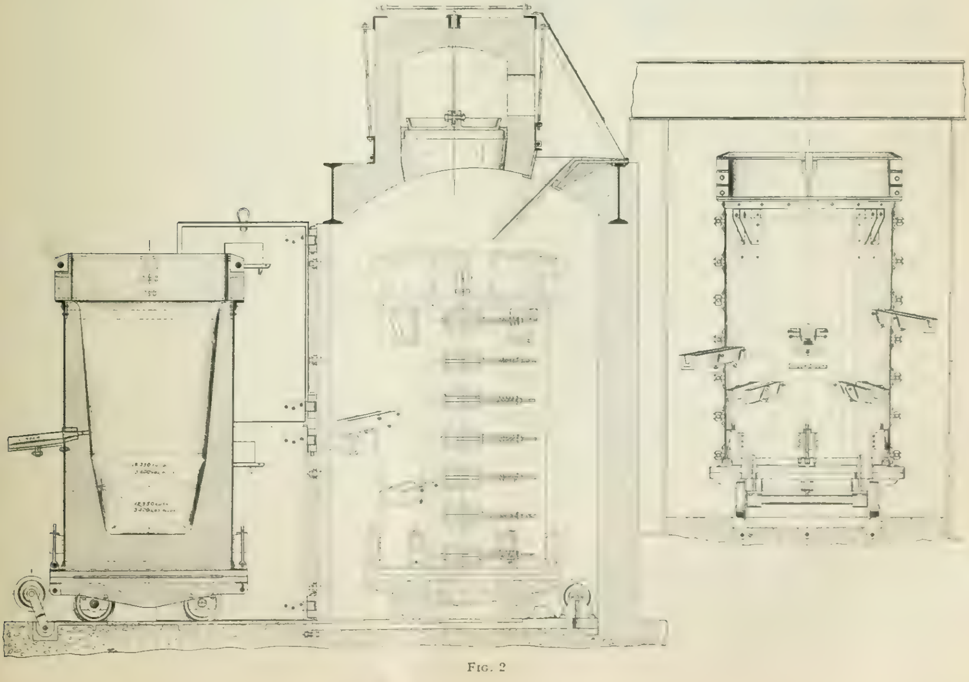

Fig. 2

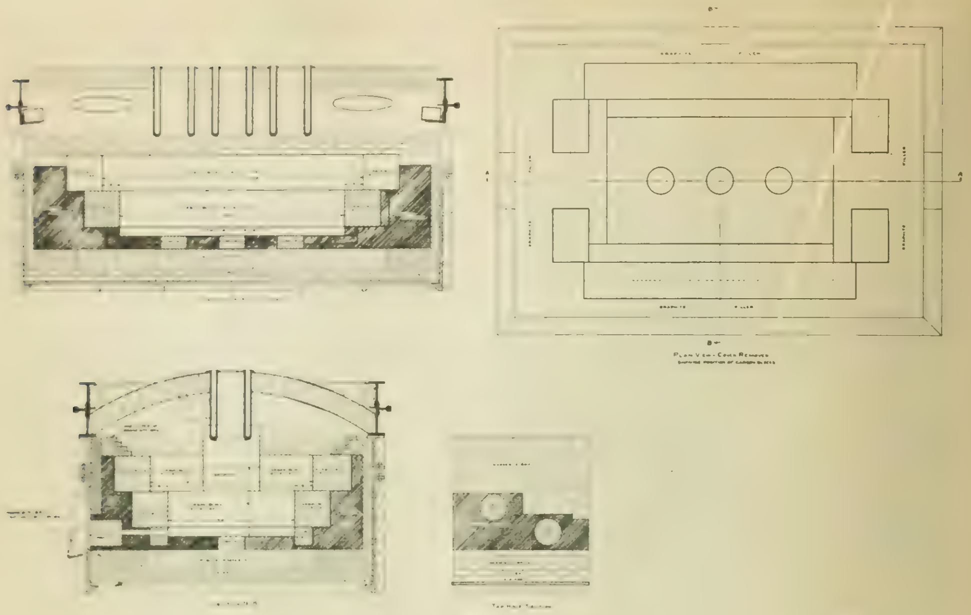

Fig. 3

Treatment of Vanadium Ores

The main industrial processes for the treatment of vanadium ores can be divided into two main groups; wet leaching processes and dry smelting operations. The first group can be subdivided into acid and alkaline processes. In the acid process the ore is treated with sulfuric acid in the presence of a reducing agent (iron turnings) to keep the vanadium in the basic stage of lower valency. The vanadyl sulfate solution thus obtained is evaporated to a sulfate cake, which in turn is calcined to an oxide, or the vanadic acid is precipitated from this sulfate solution by the action of a strong oxidizing agent, such as a chlorate or persulfate. In the alkaline leaching processes the ore is roasted with salt or soda or salt cake or a mixture of them. The vanadate thus formed is extracted with water. From this solution the vanadic acid is precipitated by the addition of a mineral acid, such as sulfuric. A method of electrolytically precipitating the vanadic acid from the vanadate solution has also been suggested.

The losses connected with the wet leaching processes have practically made them obsolete. The dry smelting processes applied to the ores directly were based on the principle of matte smelting. The ore, containing sulfur, or with native sulfur added to it, was smelted with appropriate fluxes in a reverberatory furnace, whereby all the heavy metals contained in the ore, such as iron, manganese, nickel, copper, lead, arsenic, or antimony, were converted into a matte, leaving the vanadium separated into the slag, from which it was reduced to the alloy.

Reduction

The inherent difficulties in the metallurgy of vanadium, rendering the extraction of this metal costly and wasteful, and also the most marked advances in the last few years, are to be found in the last stage of reduction to the metallic state of the vanadium compounds obtained by the wet or dry processes, or of the ores without such preliminary processes.

Vanadium usually exists in the materials to be reduced in the pentavalent state. The temperature at which reduction of the vanadium oxide starts is extremely high, probably higher than that for any other metal known, with the possible exception of uranium. On the other hand, pentavalent vanadium reduces to the tetra- or trivalent condition extremely readily. If, therefore, a mass of vanadium pentoxide in intimate contact with a reducing agent, is brought gradually to a higher temperature, with the successive increments of temperature the valency of the original mixture will gradually change, so that when the temperature of reduction is reached the reducing agent will no more be acting on pentavalent vanadium, but on a mixture of different valencies. Now some of the lower oxides of vanadium, such as V_2O_4, are extremely refractory and practically infusible and irreducible. Instead of reducing to metal, such compounds will therefore combine with the products of oxidation of the reducing agent, fluxes, etc., and be lost.

It is apparent that this difficulty can be obviated if the reduction temperature can be produced instantaneously, and no opportunity afforded the V_2O_5 to form lower oxides, prior to reduction to metal. This condition is ideally satisfied in the case of alumino-thermic reduction. Consequently this method of reduction has played a very significant part in the early development of vanadium metallurgy. As is well known, this reaction consists in subjecting a mixture of grained aluminium and an oxide to the reduction temperature, whereby an instantaneous interaction takes place, the aluminium combining with the oxygen of the oxide, forming a slag, and the metal separating as a regulus. This method, in the case of pure oxides and carried out on a small scale, is an extremely simple operation. However, when the principle is applied to a complex ore carrying several metals and gangue elements, it presents difficulties not encountered in any other metallurgical operation. In the smelting of ores by ordinary furnace processes the undesirable elements are eliminated by the production of a slag with suitable fluxes. We know that for the production of such a slag, besides the chemical constituents, the physical conditions in the furnace play a big part. We therefore have, for example, a close temperature control of the operation, and also provide delicate means whereby we can control temperature to a very fine degree. In the alumino-thermic reduction of complex ores we are working without the aid of such extraneously controllable physical means. The temperature is dependent only on the chemical reaction taking place, and consequently mainly on the amount of aluminium oxidized per unit of time. This amount, however, is governed by the constituents of the ore subjected to reduction. Fluxes are added to slag off the impurities. These fluxes retard the temperature of the reaction if they form an endothermic slag. The means employed to control at will the alumino-thermic reduction of complex ores consist in (1) adding highly oxygenated compounds, such as sodium nitrate, which increase the oxygen content of the mixture without adding any metallic constituents in the alloy, (2) increasing the temperature by increasing the rate of feed of the mixture, (3) making the particles of the constituents finer, or (4) increasing the scale on which the reaction is carried on so that with large masses treated there will be an accumulation of heat energy stored as the reaction continues. To summarize these remarks it may be said that in the calculation of the mixture for reduction such a balance has to be found among the ingredients as will produce not only the right compounds in the slag and the right elements in the metal, but also the right amount of exothermic energy per unit of time, capable of keeping such slag and metal in the perfect fluid condition necessary for their separation. It is easy to see that this reduction process presents problems not ordinarily met. In the development of the vanadium industry it has been worked out to an extent as to form practically a new branch of metallurgy.

Fig. 1 shows diagrammatically the evolution of this process, where for the purpose of obtaining better control of temperature and reaction the capacity of the reducing crucible was increased from about 30 to 35 lbs. to 7800 lbs. of alloy. This figure also shows several types of crucibles or furnaces developed for alumino-thermic reduction. Fig. 2 shows in detail the mechanism of the type of reducing crucible finally evolved with the feeding arrangement, tapping spouts, etc.

In spite of the development of alumino-thermic reduction to a high degree, several factors in connection with the development of vanadium metallurgy, such, for instance, as the high cost of aluminium as a reducing agent, have necessitated the employment of other means of reduction. Since Moissan's unsuccessful attempts in 1893–94 to reduce vanadium by carbon in the electric furnace, several processes of electric reduction have been suggested, involving such metallic reducing agents as silicon, manganese, silicon carbide, calcium carbide, boron, or boron carbide. Of these processes only the reduction with silicon has appeared to be of any commercial interest. It has, however, in common with the aluminium reduction, the inherent defect of high cost.

The reduction of vanadium by means of carbon on a commercial scale has, however, been successfully accomplished within the last couple of years. The theory of instantaneous reduction, which made the aluminium reduction process successful, has been transferred to the electric operation. Physical conditions of alumino-thermic reduction are reproduced electrothermally, principally a localized zone of extreme high temperature into which the mixture of ore, reducing agent, and fluxes is fed. This mixture reacts instantaneously, owing to the high temperature, is converted into slag and alloy, and passes out of the reacting zone to make room for the next portion of mixture arriving in the high temperature zone. The high degree of heat is obtained by the employment of high voltage and current density, combined with close spacing of electrodes, producing more or less a blow-pipe effect. The mixture is fed continuously in the hottest part between the electrodes. The furnace is a three-phase rectangular furnace with a water-cooled cover, furnished with water-cooled bushings for three 12-in. graphite electrodes. The mix is fed in the furnace through water-cooled bushings in the top of the cover by means of continuous automatic feeders, and the metal and slag are tapped off by means of appropriate spouts.

Fig. 3 shows a sectional diagram of one 4000-kw. furnace. Fig. 4 shows the general exterior arrangement of the furnace installation.

VANADIUM ALLOYS

Vanadium has also entered the field of nonferrous metallurgy, and several alloys have been marketed for use in the nonferrous industry. A cuprovanadium, an aluminovanadium, a manganovanadium, and a cupromanganovanadium are commercial alloys. The exploitation of vanadium in the nonferrous industry is, however, comparatively in its infancy and furnishes a fertile field for metallurgical research.

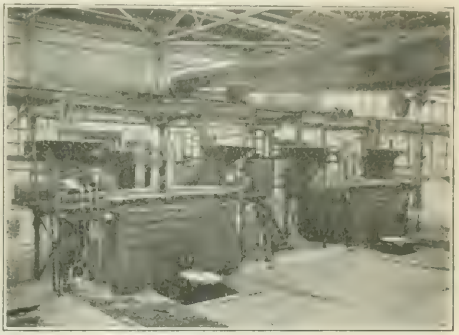

FIG. 4

POSSIBILITIES FOR VANADIUM RESEARCH

Another metallurgical phase which has received little attention is the production of the metal itself without being alloyed. The production of pure metallic vanadium has been one of the most difficult problems of experimental chemistry. Its high temperature of reduction and chemical activity are responsible for this. All early attempts to produce pure vanadium have failed. Roscoe undertook reduction of the chloride by hydrogen. Setterberg attempted reduction with sodium. Goldschmidt failed to produce pure vanadium by means of aluminium. Weiss and Aichel tried reduction of the oxide by means of *Mischmetal*, a mixture of cerium, lanthanum, and other rare metals. Prandtl and Bleyler failed in reduction with metallic calcium. Ruff and Martin attempted reduction with pure carbon. Cowper-Coles did not succeed in producing pure metal by aqueous electrolysis. Werner von Bolton attempted to obtain the metal by the so-called dry electrolysis. He prepared a filament of V_2O_5 using paraffin as a binder, and subjected this filament to the electric current in vacuum in order to dissociate the oxygen away from the metal.

On account of the inability to prepare the pure metal, naturally, statements as to its physical properties are very vague. Any future developments as to methods of preparing pure vanadium might prove of great commercial value. It might lead to investigations of alloys of vanadium with some other highly refractory metals such as tungsten, titanium, uranium, tantalum, etc., which alloys might possess remarkable physical properties useful in the arts.

Apart from the metallurgical side, vanadium has suffered very little technological development. An element as chemically active and as remarkable in its varying properties as vanadium would undoubtedly find useful application in chemical technology. As an example may be suggested its use as an oxidizing catalyst in the manufacture of perchlorates and perborates, and in several organic reactions. The use of vanadyl chloride as reducer in place of stannous chloride, and of its oxygenating compounds as a bactericide in water purification may be mentioned. The strong physiological activity of vanadium will also some day be utilized in the manufacture of compounds similar to the arseno compounds, such as salvarsan. It would appear that an element capable of easy transference of valency as vanadium would open some field of research in its application to the use of electric cells, primary or secondary. The potential difference between the low and high valency compounds as measured by Marino seems to indicate that a research in this direction might be very fruitful. It is clear from these few examples that the chemical development of vanadium is still ahead of us, and it is to be hoped that its success in steel metallurgy will be the factor toward its wide application in other branches of technology.

Can We Afford the Ford?[1]

By George Granger Brown

Department of Chemical Engineering, University of Michigan, Ann Arbor, Michigan

The average Ford touring car, driven under average conditions, gives not more than 17.5 mi. per gal. Compared with other cars it should give 24 mi. per gal.

One cause for this inefficiency is the present carbureting system, which can be so improved that the average Ford, driven under average conditions, will give 25 mi. per gal. and operate as economically as more expensive cars.

If this one improvement were applied to all the Ford cars in this country, 400,000,000 gal. of gasoline would be saved annually.

Of the 11,000,000 motor vehicles in the United States about 5,000,000 are Fords. If each Ford covers annually 5000 mi., we have 25,000,000,000 Ford miles per year. At an average of about 17.5 mi. per gal. this means a consumption of over 1,400,000,000 gal. of gasoline, more than one-fourth the total production of this country. Even a small saving in the fuel consumption of Ford cars alone is well worth the effort. Every general increase of 10 per cent in the efficiency of Fords means more than 140,000,000 gal. of gasoline saved annually for future use, more than $30,000,000 to help pay the income tax, or, if you have the sales point of view, 75,000 more Fords sold per year.

The tests described in this paper indicate that the above estimates based on a saving of 10 per cent are very conservative—in fact at least 25 per cent increased mileage should be expected by making the slight changes in equipment suggested.

In making comparative tests on motor cars the utmost care must be taken to maintain all conditions, except those purposely varied, as constant as possible; otherwise the results are absolutely worthless. It is possible to obtain anywhere from 5 to 35 mi. per gal. with the same standard equipped Ford touring car, depending entirely upon the conditions under which the car is driven. In one case the car was driven through very heavy city traffic in cold weather by an "experienced" but very inexpert driver, in the other case the car was driven by a very careful expert driver, at a constant speed of about 10 mi. per hr. on a level concrete highway, on a hot humid day. The careless driver used a rich mixture, the careful driver drove a hot engine with a very lean mixture—so lean that the engine would backfire when an attempt was made to accelerate.

For the present discussion it will be convenient to consider the over-all efficiency of a motor car as consisting of two factors, the efficiency of the power plant, and the drag of the chassis and body. The power plant efficiency is determined by the design of the engine and transmission, and the effectiveness and efficiency of the ignition and carbureting systems. The drag, or dead load, of the chassis and body is roughly a function of the car weight. In order to get the best possible results it is necessary that all of these factors receive the most careful attention. The high cost of fuel in Europe has forced European manufacturers to consider these factors, and they have brought forth a number of very light cars equipped with efficient power plants of 12 to 20 h. p. These cars will run from 35 to 60 mi. per gal., depending upon conditions. Because of the low price of gasoline in the United States our motor cars are not designed for maximum economy. We have light cars with inefficient power plants and some cars with efficient power plants handicapped by a 4000- or 5000-lb. mass of dead weight.

In order to make intelligent comparisons of the relative operating economy of different cars, the variable weight and different designs must be reduced to a constant common basis. This can be done in a very satisfactory manner.

The wind resistance of all cars is practically the same. The rolling resistance, and particularly the force necessary for acceleration, is directly proportional to the weight of the car. The efficiency inherent in the power plant varies inversely as the displacement of the engine per unit of distance traveled.

These factors may be represented as follows:[2]

N = Number of cylinders
B = Bore, in in.
A = Area of bore, sq. in.
S = Stroke, in in.
H. p. = Horse power, $\frac{B^2N}{2.5}$
D = Total displacement, $\frac{ANS}{4}$
R = Gear ratio, rear axle
T = Tire
Wh = R. p. m. rear wheel @ 1 mi. per hr., $\frac{1056}{\text{Tire dia.} \times \pi}$
M = R. p. m. motor @ 1 mi. per hr., Wh × R
Wt = Weight of car, in lbs.
C = Economy constant, $\frac{1000}{\sqrt{DM(1000 + Wt.)}}$
G = Mi. per gal. under reasonably efficient operating conditions, $\frac{5200}{\sqrt{DM(1000 + Wt.)}}$

The accompanying table shows the application of this formula to a number of standard cars produced in 1921.

This table is intended simply as an estimate of the miles per

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[1] [illegible]

[2] See also C. T. Myers, *Trans. Soc. Automotive Eng.*, [2] **9** (1914), 122, and *Soc. Automotive Eng. Bull.*, **8** (1915), 257.

Car	Model	H P	N	B	A	S	D	R	T	Wh	M	Wt	C	G
American	C	25	6	3 1/4	8.296	5	62.2	4.5	32 x 4	10.5	47.25	3500	0.28	14.5
Buick	22-34-37	18	4	3 3/8	8.946	4 3/4	42.5	4.66	34 x 4	10.84	50.5	2300	0.375	19.5
Buick	22-44-47	27	6	3 3/8	8.946	4 1/2	60.4	4.6	33 x 4	10.2	47.0	3000	0.296	15.4
Cadillac[1]	61	31	8	3 1/8	7.67	5 1/8	78.6	4.44 (?)	33 x 5	10.2	42.1 (?)	4000	0.245 (?)	12.7 (?)
Chalmers	6-30	25	6	3 1/4	8.926	4 1/2	56.0	5.12	32 x 4	10.5	53.75	2800	0.295	15.3
Chandler	Six	29	6	3 1/2	9.621	5	72.15	4.4	33 x 4	10.2	41.9	2985	0.278	14.5
Chevrolet	490	21	4	3 11/16	10.68	4	42.7	3.66	30 x 3 1/2	11.2	41.0	1800	0.45	23.1
Dodge	...	24	4	3 7/8	11.79	4 1/2	53.1	4.16	32 x 4	10.5	48.1	2400	0.338	17.6
Dort	19	29	4	3 1/2	9.621	5	48.1	4.45	31 x 4	10.84	48.25	2320	0.359	18.6
Essex	...	18	4	3 3/8	8.946	5	44.7	4.66	32 x 4	10.5	49.0	2500	0.357	18.5
Ford	T	22	4	3 3/4	11.04	4	44.2	3.63	30 x 3 1/2	11.2	40.6	1500	0.472	24.6
Franklin	9B	25	6	3 1/4	8.296	4	49.8	4.33	32 x 4	10.5	45.5	2430	0.359	18.6
Haynes	55	29	6	3 1/2	9.621	5	72.15	4.11	33 x 4	10.2	42.0	3200	0.28	14.5
Hudson	...	29	6	3 1/2	9.621	5	72.15	4.81	34 x 4 1/2	9.88	47.5	3500	0.254	13.2
Hupmobile	R	16	4	3 1/4	8.296	5 1/2	45.6	4.87	33 x 4	10.2	49.7	2500	0.344	17.9
Lincoln[1]	...	36	8	3 3/8	8.946	5	89.45	3.71 (?)	33 x 5	10.2	36.8 (?)	4100	0.244 (?)	12.7 (?)
Locomobile	48	48	6	4 1/2	15.9	5 1/2	131.2	3.8	35 x 5	9.6	36.4	5300	0.182	9.5
Marmon[1]	34	33	6	3 3/4	11.04	5 1/8	84.9	4.1 (?)	32 x 4 1/2	10.5	40.3 (?)	3800	0.238 (?)	12.4 (?)
Maxwell	...	21	4	3 5/8	10.32	4 1/2	46.45	4.56	31 x 4	10.84	49.5	2100	0.374	19.4
McFarland	TV	48	6	4 1/2	15.9	6	113.1	3.5	33 x 5	10.2	35.7	4800	0.184	9.5
Mercer	5	22	4	3 3/4	11.04	6 3/4	74.55	3.87	32 x 4 1/2	10.5	40.6	4000	0.257	13.3
Mitchell	F50	29	6	3 1/2	9.621	5	72.15	4.42	33 x 4	10.2	45.0	3400	0.264	13.7
Nash	682	25	6	3 1/4	8.296	5	62.2	4.5	33 x 4	10.2	45.9	3000	0.296	15.4
Nash	41-4	16	4	3 3/8	8.946	5	44.7	4.5	33 x 4	10.2	45.9	2500	0.372	19.4
Oakland	6-44	19	6	2 13/16	6.213	4 3/4	44.25	4.66	32 x 4	10.5	49.0	2300	0.373	19.4
Oldsmobile	43 A	21	4	3 11/16	10.68	5 1/4	56.1	4.66	32 x 4	10.5	49.0	2700	0.313	16.2
Oldsmobile	46	26	8	2 7/8	6.492	4 3/4	61.7	4.93	33 x 4 1/2	10.2	50.3	3150	0.278	14.5
Overland	4	18	4	3 3/8	8.946	4	35.8	4.5	30 x 3 1/2	11.2	50.5	1900	0.435	22.6
Packard-single	...	27	6	3 3/8	8.946	4 1/2	60.4	4.3	33 x 4 1/2	10.2	43.9	2900	0.311	16.2
Packard-twin six	...	43	12	3	7.069	5	106.0	4.36	35 x 5	9.6	42.0	4170	0.202	10.5
Paige	644	25	6	3 1/4	8.296	5	62.2	4.75	32 x 4	10.5	50.0	3000	0.282	14.7
Paige	666	33	6	3 3/4	11.04	5	82.85	4.55	32 x 4 1/2	10.5	47.8	3500	0.236	12.3
Pierce Arrow[2]	33	48	6	4	12.57	5 1/2	103.7	(?)	33 x 5	10.2		5100		
Reo	T 6B	24	6	3 3/16	7.98	5	59.85	4.7	33 x 4	10.2	48	3100	0.291	15.1
Stevens	SkL4	22	4	3 3/4	11.04	5 5/8	62.1	4.5	34 x 4 1/2	9.88	44.5	3600	0.28	14.5
Studebaker-Light[2]	...	23	6	3 1/8	7.67	4 1/2	51.8	(?)	32 x 4	10.5		2500	.	.
Studebaker-Special[2]	...	29	6	3 1/2	9.621	5	72.15	(?)	32 x 4	10.5	..	2900	.	.
Studebaker-Big[2]	...	36	6	3 7/8	11.79	5	88.45	(?)	33 x 4 1/2	10.2	..	3200		
Willys Knight	20	21	4	3 5/8	10.32	4 1/2	46.45	5	33 x 4	10.2	51.0	3000	0.325	16.9

[1] Gear ratio rear axle not certain.
[2] Gear ratio rear axle unknown.

gallon obtained with different cars driven with the same operating efficiency, and should not be used unless this condition is fulfilled. A large number of tests have demonstrated the fundamental accuracy of these estimates as a basis for comparing the operating efficiencies.

The reasonable mileage of a Ford touring car is given as 24.5 mi. per gal., yet the average obtained throughout the country is not more than 17.5. The latter, for example, would correspond to 12 mi. per gal. for a Franklin, Essex, or a Dort. Franklin cars will average about 18 or 19 mi. per gal. It is just as easy to get 25 mi. per gal. from a Ford as 19 mi. from a Franklin, yet it is not done for the simple reason that the Ford car is not properly equipped for efficient operation. One cause of inefficiency is the standard carbureting system (low in first cost but expensive to operate), which can give satisfactory results only when the engine is running hot and when the adjustment is constantly changed by an expert to suit speed, throttle, and road conditions.[3] Under these particular conditions, 22 to 24 mi. per gal. can be obtained under steady driving. But the average driver is not expert, and he could not use the dash adjustment to the best advantage even if he would.

An official economy test run on May 14, 1913, from Weehawken, N. J., to Newburgh, N. Y. (64.7 mi.) resulted as follows:

Car	Weight	Gal. of Gasoline	Mil. per Gal.	Relative Fuel Consumption
Ford	1614	3.33	19.3	206
Paige	2500	4.056	15.9	162
Pathfinder	2790	5.301	12.1	190
Briggs	2460	4.324	14.9	175
Oakland	2680	5.482	11.8	204
Mercer	2540	5.000	12.9	196
American	3800	7.503	8.57	197
Alco	4630	8.726	7.38	188

Best Score—162 by Paige
Poorest Score—206 by Ford

On June 11, 1914, this same course was covered by a standard equipped Ford similar in every respect to the one used in the above test, except that it was not in perfect condition, having been in general use for some time and not overhauled or specially prepared for a test in any way. After covering the distance to Newburgh, the car was brought back to Weehawken and equipped with an improved carburetor.[4] No other changes or adjustments of any kind were made. The following day, June 12, 1914, the same Ford car was driven over the same course by the same driver with the following comparative results.

Weehawken to Newburgh, 64.7 mi.

	Gal.	Mi. per Gal.	Relative Fuel Consumption
Ford, standard carburetor	3.68	17.6	228
Ford, improved carburetor	2.52	25.7	156
98 mi. on LongIsland (August 1914)			
Ford, improved carburetor	3.9	25.25	158

The car was then put through the shop and found to have a faulty timer. After the car had been put into first-class condition in every respect, 20 mi. per gal. could be obtained with the standard carburetor and 29 mi. per gal. with the improved carburetor.

These results, which have been repeatedly checked in the last eight years, show a 45 per cent increase in mileage, or a 30 per cent decrease in fuel consumption, by simply supplying an improved carburetor to a standard Ford touring car, that the Ford car can be made to operate as efficiently as the more expensive cars by simply supplying a satisfactory carbureting system. They show that you can drive your Ford 7250 mi. on the same amount of gasoline you now use for 5000, that Ford could buy a Muscle Shoals every 18 days with the savings made by improving the carbureting system on his cars which are wasting annually 400,000,000 gal. of gasoline, $100,000,000; every week more than enough to adequately support the Chemical Warfare Service for a year! Can we afford it?

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[3] For a discussion of the variables affecting economy and engine performance, see "A Chemically Controlled Automobile," This Journal, **14** (1922), 6.

[4] Similar to the carburetor described in "A Chemically Controlled Automobile," *Loc. cit.*

An institute of theoretical and applied optics with a course lasting two years has been established at Paris. A research laboratory is an important part of the institute. A monthly journal has been established, *Revue d'Optique théoretique et instrumentale*, which has the coöperation of the French syndicate of makers of optical apparatus and instruments of precision.

John D. Rockefeller, Jr., has agreed to donate $60,000 to Princeton University for the establishment of a Library of Industrial Relations.

Chemistry in the Senate

Importance of the Science Emphasized by Prominent Senators

(Excerpts from Congressional Record of August 17, 1922)

On August 17, 1922, in discussing the Bursum Amendment, several senators spoke in favor of it. Senator Bursum of New Mexico in presenting the amendment began by saying:

> Mr. President, the serious question confronting the country at this time, which prompted the introduction of this amendment, is whether the dye industry of this country shall be permitted to live, whether it shall be preserved, or whether we will permit it to go on the rocks, and depend upon Germany, as we did prior to the war, for our supply of dyes.

Senator Sterling of South Dakota, after declaring himself in favor of the amendment and explaining his preference for an embargo, said:

> But, thinking that the embargo may not carry in the Senate, I am in favor of the amendment of the Senator from New Mexico.
>
> I want to call attention just briefly to two or three facts and then cite some authorities which I think ought to have a controlling influence in this discussion.
>
> It has been charged, of course, that there was great danger of a combination; that there was an actual combination between the dye-industry people. I have the honor of being a member of the sub-committee of the Judiciary Committee which investigated the dye industry. I was unable to hear all the testimony; very much of it I could not hear because of other pressing duties, but that which I did hear convinced me that there was no combination whatsoever among the various dye industries in this country. Indeed, the witness most relied upon by those who were asserting that there was a combination or monopoly admitted that there was the sharpest competition between the various companies engaged in the production of chemicals and dyes. That witness was Mr. Metz.

He then continued, citing a number of authorities such as Mr. James Morton, chairman of the Scottish Dyes, Ltd., to free trade members of Parliament, and Mr. Taussig, formerly a member of the Tariff Commission. He concluded:

> Mr. President, I think I have not much more to add. I feel that interest in this very great and important industry. It has done so much within the short time it has been in existence since the beginning of the war, produced so much of wealth for the United States, given employment to so many thousand workmen, skilled and unskilled, in the United States, it seems to me that as American citizens, with pride in our industrial development, we should maintain and encourage it in the highest possible degree.

Senator Ransdell of Louisiana then spoke convincingly as follows:

> Mr. President, I favor strongly the amendment of the Senator from Arizona. It seems to me, sir, that it has in it more possibilities for good to America and the world than any other feature of the bill. In considering this amendment we must bear in mind how necessary it is to establish and maintain a strong chemical industry in America, how essential this industry is for our welfare, our national defense, and, in a more important way, our public health.
>
> The Germans, through their investigation of coal-tar products, have developed some marvelous remedies as an incident to the dye industry. They discovered and placed on the market salvarsan, which cures one of the most loathsome and terrible diseases that ever afflicted the human race. They discovered novocaine, one of the greatest deadeners of pain known to science, wonderful in that it is a nonhabit-forming drug, a most beneficial thing. Many other very helpful drugs have been developed by the efforts of the German chemists in connection with coal tar.
>
> I cannot believe, sir, that the wise men of Germany have even scratched the surface of the possibilities of the coal-tar industry. Coal, sir, was made by the great Chemist of nature, how many years ago none of us know, and in its manufacture everything that grows out of the ground, I imagine, was used, the most exquisite flowers, the sweetest balsams, the most healing plants and herbs of every kind and sort, and vast forests of giant trees. Coal furnishes more commodities for the use and health and comfort of mankind than anything I know of. The wonderful violet and rose perfumes which our ladies use are manufactured from coal. Saccharine, which is five hundred times as sweet as sugar, is manufactured from coal. All the beautiful dyes we admire so much are manufactured from coal. I could tell about many wonderful things, but have not time or opportunity to do so.
>
> It seems, sir, that we should encourage in America in every possible way this enterprise which the Germans have set on foot and from which so much benefit has come to mankind. Does anyone believe that Germans have all the wisdom of the world? Does any American doubt that our composite American population is as wise and contains as smart people as Germany? Does anyone doubt that under proper encouragement American chemists will develop just as many valuable things from coal tar as have the Germans? As the German chemists have discovered novocaine and aspirin and salvarsan, why cannot American chemists discover remedies for cancer and leprosy and that most fatal of all diseases—tuberculosis? Great efforts to that end have already been made by American chemists. Let us encourage them in every possible way. American doctors have in the last 25 years demonstrated that they can do wonders in treating diseases. American doctors discovered the cause of hookworm and pellagra and treated them successfully. They found out that the Stegomyia mosquito was the cause of yellow fever and have practically eradicated that dread disease throughout the world. All we need to do, sir, is to give proper encouragement to American chemists and they will, in my judgment, prove by their medicinal discoveries just as beneficial to America and to the world as ever the Germans have been, and as helpful to suffering humanity as their brethren in the medical profession, for I cannot believe that all the secrets in the interest of health hidden by the Architect of the Universe when He created coal have yet been unearthed. There are many secrets still hidden. Let us discover them, or at least let us try to discover them. This is only one phase of the case.
>
> Many people say, and I agree with them, that the next war, if war must come—and unfortunately it has always come to the world—will be a chemical war. America must be ready for it at home. She must develop her own chemical resources and not depend upon other countries. She must create a great chemical industry, and make all known combustibles in order to be prepared for a possible war.
>
> This matter of national defense is only one of many important things which can come from the development of the coal-tar industry. I sincerely hope, sir, that the amendment will be agreed to.

He concluded his remarks by reading into the Record an excellent letter from Councilor Charles E. Coates of the Louisiana Section of the American Chemical Society.

Then followed remarks by Senator Wadsworth of New York which we quote in full:

> Mr. President, as a part of my remarks, I ask that a letter written by the Secretary of War to the chairman of the Committee on Finance, the Senator from North Dakota [Mr. McCumber], may be read by the Secretary.

> The Presiding Officer: Without objection, the Secretary will read as requested.

> The reading clerk read as follows:

WAR DEPARTMENT
Washington, August 15, 1922

CHAIRMAN UNITED STATES SENATE FINANCE COMMITTEE,
Senate Office Building, Washington, D. C.

MY DEAR SENATOR MCCUMBER:

On July 26, 1921, I wrote your committee, calling attention to the fact that the Fordney tariff bill would not protect the American organic chemical industry from destruction by German competition. Allow me to reiterate

> the importance of the preservation of the industry to the country from the standpoint of national defense.
>
> The dye industry is the backbone of the organic chemical industry, on which all Governments are dependent for their high explosives, their medicines, and other materials. Inasmuch as the coal-tar industry, which is the basis of all dyes, is also the basis of all high explosives and of synthetic medicines, it is of vital importance to preparedness that the dye industry be developed to the fullest possible extent in this country. The use of explosives will be far greater in any future struggle than in the World War.
>
> Notwithstanding that from 1914 to 1917 our great steel industries and our rapidly developing chemical industries had been working feverishly to increase their facilities to supply ammunition, guns, and rifles to the Allies, it was more than a year after we entered the war before those industries were able to supply ammunition, guns, rifles, etc., to meet the American needs. Even then our chemical industry was so undeveloped in 1917 that it was necessary for the Government to build large high-explosive plants and powder factories.
>
> Germany realizes the importance of predominance in organic chemical industries as a most valuable means of preparedness and has formed of them one great trust. The German trust can produce dyes and similar material so much cheaper than the Americans produce them that no ordinary tariff can prevent the destruction of the American industry, which will thereby cripple the whole organic chemical industry.
>
> It is, therefore, urged that the dye-control provisions of the emergency tariff act of 1921 be extended another year to give the industry a chance to stabilize and to enable conditions in the dye industry to be carefully observed and the products determined which should be protected in order to firmly establish that industry in the United States.
>
> Very truly yours,
>
> JOHN W. WEEKS,
> *Secretary of War*

MR. WADSWORTH: Mr. President, it is apparent, of course, that the concluding paragraph of the letter of the Secretary of War is not applicable to the amendment which is now pending because in that paragraph the Secretary urges the continuation of the selective embargo at present in force. I thought, however, it would not be amiss that the letter of the Secretary in which he discusses from the standpoint of the national defense the value of the organic chemical industry be placed in the RECORD at this time. I think that not even the most suspicious-minded man will accuse the Hon. John W. Weeks of being impelled by unworthy motives when he urges upon Congress the consideration of the chemical industry in connection with the defense of the Republic.

It is quite possible, Mr. President, that a good many Senators do not feel as deeply upon this subject as do I. Perhaps I feel too deeply upon it; I do not know; but, such as my feelings are, I intend to express them upon this occasion as briefly as possible.

From what I have been able to learn of the history of organic chemistry in this country, especially in the dye industry, prior to our entrance into the World War, during our participation in the war, and since the war, I am convinced that long before the United States actually declared a state of war the German Government and the cartel were in effect, although slyly, waging war against the peace and the safety of the people of the United States. We did not wake up to that situation until we ourselves got into the fight. The letter of the Secretary of War points out very briefly—all too briefly, according to my view—but sufficiently for the purposes of this discussion the predicament in which this Republic of ours found itself when we were called upon to engage in our own defense.

Manipulations of the German cartel in the matter of patents, the immense influence, politically and otherwise, which they maintained in this country before the European war must now be known to every sensible man. Their effort was deliberate; it was skilful, and it was successful up to a certain point. That effort was directed toward making and keeping the American people as helpless as possible in the event of any great crisis overtaking them in which the German Government might be a party.

We went into the war and we learned the lesson at the cost of billions of dollars and many thousands of lives. We participated in the great victory and at the conclusion of the contest we asked for no territory; we asked no reparations; we asked for nothing of value to be taken from the vanquished and we received nothing. The only thing which has come to the people of the United States of material value as a result of their efforts and sacrifices in the Great War is peace and security in the future and the guaranty of self-maintained public health; not one other thing or opportunity of a material character has come to this great people of ours out of that war.

We have the opportunity, as the result of the contest, an opportunity seized upon legally to maintain our public health with our own resources and without depending upon any foreign government or any foreign cartel, corporation, or trust. We have secured the opportunity—and have secured it legally and properly as a result of our sacrifice and our efforts in the war—to maintain our national defense without depending upon any other nation, government, trust, or cartel of any kind whatsoever. That is the prospect which confronts the American people to-day.

Mr. President, I am not surprised that far-reaching efforts have been exerted in this country for the last two years once more to reduce us to that condition of comparative helplessness in which we dreamed and dreamed and dreamed in 1916. I am well aware of the influences which have been brought to bear here in Washington; I am well aware of the source of those influences; I know perfectly well that if this cartel can once more establish its domination over the organic chemical industry of the United States, such as it enjoyed prior to our entrance into the war, the enemies of America, actual and potential, will rejoice.

I question not the motives of Senators who do not see this question as I see it; without doubt they are sincere; but it passes my comprehension how they can fail to read the signs of the times. If there ever was a deliberate attempt to break down, to undermine, to weaken the power of American self-defense, it has been made in connection with the American organic chemical industry.

It does not do, Mr. President, in discussing this matter, to drag the names of American citizens into the discussion and accuse them of dishonest motives because, forsooth, they take an interest in the perpetuation of this chemical industry here in America. It does not do, Mr. President, to bring inferences and insinuations against Francis P. Garvan; not by any means. I care not what his politics are; I understand he is a Democrat; I have known him since 1895 and known him well. He is an honest man, and he has no thought in his mind or motive in his heart except the safety of this country. It does not do to bring unfair inferences and insinuations against men like Otto Bannard, of New York, who is one of the trustees of the Chemical Foundation, for he is an honest man, with no thought except the safety of his country.

I shall not discuss upon this occasion the wisdom or the unwisdom of the policy adopted by the last administration in the handling of the patents covering the dyes through the Chemical Foundation as trustee; that is not a part of this discussion; but I know full well, if I know anything about the psychology of this situation, that the attack upon the Chemical Foundation had a most material influence upon the votes cast on the question of the tariff on dyestuffs. It is for that reason that I deplored it at the time, although not publicly, for I had no opportunity to do so, but I deplore it now. It is not the question at issue.

Mr. President, as I said in my opening sentence, I feel deeply on this question. I believe that there is involved in it one great issue: America safe against attack from without and safe in the matter of public health, or America dependent upon some outside power and influence in the matter of its self-defense and in the matter of its public health.

This organic chemical industry lies at the bottom of nearly everything we use. I firmly believe that the progress of the race from now on will be measured more by the progress in organic chemistry than in any other human effort. I believe that in organic chemistry lies the solution of the secrets of the past and of the future. I believe that its establishment and maintenance in this country, even under an embargo, mean the happiness, the progress, and the security of 100,000,000 people. No rate of duty will frighten me and no embargo will frighten me.

I notice that England has put an embargo against the importation of dyestuffs. I notice that France has done the same thing. I notice that Italy has done the same thing. I notice that Japan, if she has not already done so, is about to do so. They have awakened to the significance and the importance of organic chemistry. I pray that the time will come when American public opinion will come to an appreciation of what organic chemistry means, of what research means, in the way of progress. We have been interested as a people in the development of material resources—the digging of iron and coal from the ground, the raising of crops upon the surface, and the engaging in transportation and other forms of commercial effort. As a people we have paid little attention and given little encouragement to scientific research, but, Mr. President and Senators, the progress of the future depends upon scientific research. It is the man working in the chemical laboratory who is to blaze the way for human progress.

I want to see the chemical laboratories of this country multiplied again and again. They cannot be multiplied, they cannot be maintained, no student will attempt to attend their courses unless there is a chemical industry in which those students upon graduation may find a career.

The two things—research in the laboratory and the successful conduct of a chemical industry—go hand in hand. Neither can proceed without the other.

I regret that the Senate voted down the selective embargo. I think it made a mistake. I was in the minority upon that proposition. That is my first choice as a remedy. The Senator from New Mexico [MR. BURSUM] has offered an amendment which, in my judgment, is next best. It will give some chance, at least, for the survival of this industry of ours, which already bids fair to be able to meet the demands of our people, although it has only been devoted to its task for three or four years, and research was almost unknown in this country. I think that industry will get a decent chance to survive under the amendment offered by the Senator from New Mexico. Feeling as I do upon this question, feeling that it is vital to the security and the happiness and the contentment of this great Nation, I beg for its adoption.

Senator Lodge of Massachusetts, after questioning Senator Smoot regarding the time required for making investigation on comparative costs in the United States and elsewhere, spoke briefly but with great emphasis and finality:

MR. LODGE: I have here a letter dated August 16 from the Tariff Commission, which I shall ask to have printed in the RECORD, and in which this statement is made:

> The time required for such an investigation is uncertain, but from experience gained in other chemical investigations we believe it will require from 8 to 10 months to make a satisfactory report on the subject.

During those 8 or 10 months, of course, the dyes would come in.

Mr. President, I did not mean to enter into this discussion. I took no interest whatever in the matter of rates or whether we keep out all other dyes or not. I have but one single interest in the question, which is derived from some years of experience in the Senate. I endeavored back in 1909, in conjunction with the Senator from Utah, to get some protection which would tend to give us an independent chemical production. We failed. We got into the war. We had no chemists who could furnish us with explosives and later with the gases. It was the same in England, which was then believing in the phantom of free trade. She found herself in the same condition. No one can possibly tell what that disadvantage, which weighed down upon both England and the United States, cost us in men, money, and time in the winning of the war. I made up my mind that, so far as I was concerned, I would use every effort in my power to see that the United States was never left again defenseless in that way.

I voted for the embargo when it was proposed by the Democratic Party. I voted for it during the war. I continued to vote for it when it was continued when the Democratic Party had not yet gone out of power. I voted for it for the sole reason that I wished the country to be independent in the matter of organic chemistry. No matter what it may cost, it is something that is worth any price they choose to pay to make the country independent in that direction.

Mr. President, I voted for it again for the same reason. It does not weigh with me that the dyes can come in at this price or can come in at another price. I want to do what the other countries have done who have learned something from their experience. I want this country to see to it, by tariff or embargo or in any other way, that organic chemistry in the United States is put in a position where we shall never find ourselves in the condition in which we were before. I am speaking not in the interest of any industry. I have not been approached by anybody representing an industry in that respect. I know the interests that are here. I have heard of the representatives of the German importing interests rejoicing in the lobbies here when the embargo was beaten the other day. I have taken this long interest in it for these years for but one reason, and I vote for this provision to-night for but one reason, and that is national defense and safety.

Chemistry Courses at College of the City of New York

The members of the Evening Session Chemical Society of the College of the City of New York would like to call the attention of chemists and students of chemistry, who wish to increase their knowledge of the subject, to the excellent opportunities offered evenings by the Chemical Department of the College. Courses are given leading to the degrees of B.S. and Ch.E. Besides these degrees, a special departmental certificate is given to students who desire chemical knowledge only. To receive this certificate the student must complete Courses 1, 2, 3, 4, 11, 20, 33, 44, 50, 55, and 70, with an average of 80 per cent, and make a satisfactory report on some research problem the student has worked on Chemistry 100. Thus, this certificate indicates that the holder has a knowledge of the main branches of chemistry (with a very good scholarship rating) and some practice in research and should be of great value to any man.

The following courses will be given this fall:

CHEMISTRY 1, 2. GENERAL DESCRIPTIVE CHEMISTRY. 6 hours per week. 2 terms. Laboratory deposit $10 per term.

CHEMISTRY 3. QUALITATIVE ANALYSIS. 7 hours per week. 1 term. Laboratory deposit [illegible]

CHEMISTRY 4. QUANTITATIVE ANALYSIS. 8 hours per week. 1 term. Laboratory deposit [illegible]

CHEMISTRY 20. PHYSICAL CHEMISTRY. 7 hours per week. 1 term. [illegible]

CHEMISTRY 33. ADVANCED QUALITATIVE ANALYSIS, mainly on rare [illegible] 1 term. Laboratory deposit $14

CHEMISTRY 44. ADVANCED QUANTITATIVE ANALYSIS. 12 hours per week. [illegible]

CHEMISTRY 50. ORGANIC CHEMISTRY, ALIPHATIC COMPOUNDS. 7 [illegible]

CHEMISTRY 55. ORGANIC CHEMISTRY, AROMATIC COMPOUNDS. 8 hours per week. [illegible]

Besides these regular courses, two or possibly three special courses of interest to specialist and graduate student will be announced [illegible]

CHEMISTRY 159. FOOD INSPECTION AND ANALYSIS. Dr. Breithut. Special practice in analysis of food products and drugs—as, milk, butter, cereals, beverages, [illegible] controlled by the city. Occasional lectures and excursions in coöperation with the Food and Drug Inspection Laboratory of the Department of Health.

CHEMISTRY 269. ECONOMICS OF CHEMISTRY. 5 hours; lectures, library and seminar. Fee $12.50. Dr. Breithut. The economics of production and distribution of chemical products, sources of new material, sources of energy, and conservation of waste. Study of consular reports and use of the Wolcott Gibbs, Chemists' Club, and New York City Libraries.

CHEMISTRY 146. TECHNICAL ANALYSIS. 8 hours of laboratory. (To be announced.) Analysis of coal, soap, paint, lubricating oils, greases, cements, asphalt, and other materials purchased by the city.

To students pursuing a degree, there is no tuition charge. Others will have to pay at a rate of $2.50 per hour per week each term. For example, a 3-hour a week subject costs $7.50 per term. Further information may be obtained by writing to the Evening Session Office, Room 226, College of the City of New York, Convent Ave. and 140th St., New York City. Registration for the fall starts Monday, September 18, at 7:00 P.M. First recitation, September 28. Students, especially for the special courses, are advised to register early, as these courses must have a certain minimum of students in order to be given.

Motion Picture Film Service

It has frequently been brought to the attention of THIS JOURNAL that professors, instructors, and others want to use moving picture films for instruction and for entertaining on many occasions, but are not familiar with the sources of obtaining films to suit their needs. Therefore, it is proposed to devote a small space each month to listing films which may prove of interest and value to our readers, including information as to source, terms, etc. We plan to begin this service with the November issue, and hope that it may prove to be of material assistance.

The Union Sulphur Company has bought from the Texas Exploration Company the sulfur deposits at Damon Mound, Texas, comprising about 215 acres estimated to contain over 14,000,000 tons of sulfur, and is to build complete mining, refining, and terminal plants.

AMERICAN CONTEMPORARIES

Beginning with this issue we shall occasionally publish intimate sketches of our prominent American contemporaries in chemistry. This plan has been inaugurated in response to the wishes of our younger people who have had no opportunity to know the personality of many men whose names are familiar to all chemists.

These sketches, then, will be short statements intended to portray something of the kind of men these chemists are, what they set out to do, and a little of what trend their life's work has taken. We wish you could meet and talk with all these folk who have had such a guiding influence upon our science in America! But that may not be possible, and so we hope these sketches, prepared by close friends for us, may in some measure meet the need. The list has been made up with the help of our staff correspondents, but may be considerably extended.

Make it a point to meet these men of chemistry through our pages if you cannot in person. [EDITOR.]

Charles Frederick Chandler—Dean of American Chemists

C. F. CHANDLER

PROFESSOR Chandler is the original exponent of the strenuous life. He was living a strenuous life as a professor in Union College and in preparation for his distinguished career as a chemist, the year Theodore Roosevelt was born.

Charles Frederick Chandler was born in Lancaster, Mass., December 6, 1836. He came from good old New England stock, attended the public schools in Lancaster and New Bedford, and studied at Lawrence Scientific School, Harvard. Ambitious to become a chemist and endowed by inheritance with Yankee pluck, he went to Europe on a sailing ship in the early fifties to continue his studies under the great masters: Hosford, Wöhler, Gustave and Heinrich Rose, Weber, Dove, and Magnus. A doctor of philosophy from Göttingen, and a full professor in Union College, at the age of twenty-one!

The day after he cast his vote for Abraham Lincoln, Professor Chandler joined Professor Egleston and General Vinton in New York, to establish what is now the School of Mines, Engineering, and Chemistry, Columbia University. He served this great institution as professor of chemistry for forty-six years, and as administrative dean of the school, for thirty-three years. He led its development from a vacant room in the basement of the old Columbia College in Forty-ninth Street, to the present great architectural group of laboratories at Morningside Heights, and placed its graduates in charge of mining, manufacturing, transportation, and construction enterprises in every quarter of the world.

Professor Chandler's educational achievements were not limited to the School of Mines. His genius was directed to building up the College of Physicians and Surgeons, which he served as professor of physics and chemistry, and the New York College of Pharmacy, as professor of chemistry, and finally as president.

Yet his energy and versatility were not at an end. His greatest public service was in the application of his scientific knowledge and genius for organization to public welfare and health. As chemist and finally as president of the New York Board of Health, he investigated and regulated gas nuisances, offensive trades, sludge acid pollution, city slaughter houses, water and milk supplies, adulterated foods and drugs. He reformed tenement house plumbing, improved ventilation, reorganized street cleaning, and established the system of visiting physicians and free vaccination. He was a pioneer in pure food and drug legislation.

Dr. Chandler is America's first and most distinguished industrial chemist. His expert knowledge and advice made him an important factor in the building up of the sugar, petroleum, gas, photochemical, textile, electrochemical, chlorine, aluminium, and many other notable American industries. He invented and introduced the assay-ton system of weights used in every smelter in America. The title, "Dean of American Industrial Chemists," is his by unanimous consent.

Professor Chandler is the recipient of many honors, official, academic, public, and professional. He has represented the federal government on many important commissions. He has received honorary degrees from numerous colleges, including an anniversary degree from Göttingen, and that of Doctor of Science from Oxford. He is a member of the National Academy of Sciences, past president of the American Chemical Society, The Chemists' Club, and the Society of Chemical Industry. Last and most important of all, he is the recipient of the Perkin Medal "for such valuable contributions to applied chemistry that he has placed the entire world in his debt, and brought added prestige and dignity to the profession of which he is such a conspicuous ornament."

Twelve years ago, when Doctor Chandler retired from Columbia, he stated that "it is much better to withdraw from active service while one is in the full enjoyment of health and strength, than wait until the infirmities of age make it evident to all that one has outlived his usefulness." Fortunately for the chemical profession and its industrial dependents, this condition has not yet arisen. Professor Chandler may be found to-day at his desk in the offices of the Chemical Foundation, or at his library, actively and enthusiastically giving the touch of a master hand to the technical problems of American industries.

M. C. WHITAKER

SCIENTIFIC SOCIETIES

A. C. S. Division and Section Meetings

DIVISION OF AGRICULTURAL AND FOOD CHEMISTRY

The symposium on "Edible Fats and Oils," conducted jointly with the Division of Biological Chemistry, was a great success. The first portion, on the manufacturing and technical phases of the subject, was presided over by David Wesson, while that of a biological and physiological nature, presented in the afternoon, was conducted by R. Adams Dutcher. The papers on rancidity promoted much discussion. The two papers on the effect of shortening as used in the baking industry were much appreciated. The five papers on the biological study of the subject drew large audiences, about 90 being present at times. Seven papers on the program were read by title only, because of absence of the authors or incompleteness of the investigations.

At the next meeting of the Division a symposium on "Insecticides and Fungicides" will be held, and one year hence it is planned to have a joint symposium with the Fertilizer Division on "Fertilizer and Crops."

The officers for next year are:

Chairman: H. A. Noyes.
Vice Chairman: R. H. Carr
Secretary: C. S. Brinton.
Executive Committee: T J Bryan, H. F. Zoller.

C. S. Brinton, *Secretary*

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DIVISION OF BIOLOGICAL CHEMISTRY

On Wednesday this Division joined with the Division of Agricultural and Food Chemistry in a symposium on "Edible Fats and Oils." The report of this very interesting symposium will be found in the report of the Division of Agricultural and Food Chemistry.

As Chairman H. B. Lewis was unable to attend the meeting, Secretary J. S. Hughes presided at the Thursday session and J. F. Lyman was elected secretary *pro tem*. At this session 21 of the 31 papers listed on the program were presented and discussed, the remaining papers being presented by title.

The following officers were elected for next year:

Chairman: J. S. Hughes.
[illegible] W. A. [illegible]
Executive Committee: H. B. Lewis, *Chairman*, A. W. Dox, D. B. Jones, A. R. Lamb, J. F. Lyman.

J. S. Hughes, *Secretary*

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DIVISION OF CHEMISTRY OF MEDICINAL PRODUCTS

In addition to the regular program of the Division a symposium on "Development of American Synthetic Medicinals" was held. The papers and discussions in the course of this symposium indicated the rapid strides being made to establish a purely American medicinal chemical industry, not only by developing the manufacture of substances already known, but by producing new superior products as well.

After the meeting program the following officers were elected:

Chairman: Edgar B. Carter
Secretary: E. H. Volwiler.
Executive Committee: C. E. Caspari, Oliver Kamm.

E. H. Volwiler, *Secretary*

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DIVISION OF CELLULOSE CHEMISTRY

The Cellulose Section was given definite status as a Division and the first meeting on the new basis proved to be of unusual interest. Wednesday afternoon was devoted to a symposium on "The Nature of Wood Cellulose." The discussion was particularly spirited and participated in by a large number of members. The symposium on "The Adsorption of Salts by Cellulose" also attracted much interest. These symposiums were so successful that many expressed the hope that others, on equally timely subjects, might be arranged for future meetings.

Of special interest to all members of this Division is the announcement of C. J. West, of the National Research Council, Washington, D. C., that, through the courtesy of the publishers of the various cellulose and paper magazines of the world, he is in a position to loan to members of the Cellulose Division current copies of practically any pulp and paper magazine, as well as articles on cellulose. He also offered to furnish photostat copies of practically any article on cellulose chemistry or pulp- and paper-making since 1909. This is a very generous offer and much appreciated by the members of the Division.

The Viscosity Committee of the Cellulose Division reported a method for the determination of the viscosity of cellulose ester solutions. This method was adopted as the tentative standard method of the Division. The details will be published in This Journal and it is hoped that a number of laboratories will report on the actual working of the method at the next meeting.

The officers elected for the Division are:

Chairman: G. J. Esselen, Jr.
Vice Chairman: L. E. Wise.
Secretary-Treasurer: L. F. Hawley.
Executive Committee: Harold Hibbert, J. F. Waite.

G. J. Esselen, Jr., *Secretary*

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DIVISION OF DYE CHEMISTRY

The meeting opened with a symposium under the leadership of R. E. Rose, on the subject of "Standardizing and Testing of Dyes." As a result of the discussion in this symposium a committee was appointed to consider the best methods of securing uniformity and correctness of results in testing of dyes as an aid to both manufacturer and user. R. E. Rose is chairman of this committee, and the other members are: L. A. Olney, W. M. Scott, J. Merritt Matthews, and J. A. Ambler.

The regular program included papers on the manufacture, properties, and application of dyes. M. L. Crossley's paper on the relation of chemical constitution and color attracted considerable attention.

Officers for the ensuing year were elected as follows:

Chairman: W. J. Hale.
Vice Chairman: R. E. Rose.
Secretary: R. Norris Shreve.
Executive Committee: L. A. Olney, L. F. Johnson.

R. Norris Shreve, *Secretary*

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DIVISION OF FERTILIZER CHEMISTRY

A special symposium had been arranged to bring out the modern trend in all branches of the fertilizer industry in the following directions: (1) Fertilizer Plant Construction; (2) Fertilizer Plant Operation; (3) Chemical Control in the Fertilizer Industry; (4) State Fertilizer Control; (5) Fertilizer Legislation; (6) Fertilizer Experimentation.

These papers described in an interesting manner the part chemistry has played in reaching the present high development of the fertilizer industry, the largest of the heavy chemicals industry. While it might at first seem that plant construction and operation are out of place in such a program, such is not the case as the relation between the type of construction and the operation and the method for the chemical control of such operation is very close and interdependent.

Several papers were presented on methods of analysis for the determination of phosphoric acid, nitrogen, and potash. Many of the possible errors in the application of these methods were discussed, together with precautions necessary to avoid them.

Several papers described and discussed fertilization experiments, the action of fertilizers in the soil and the relation of fertilizer to plant composition.

Some of the effects of the rational use of fertilizers, such as larger yields and better quality of crop, especially fruits, were described. It is becoming more apparent that the best results in the use of fertilizers are obtained from the use of sufficient quantities of properly balanced, high-grade, complete fertilizers.

The officers of this Division were reëlected for the ensuing year.

H. C. Moore, *Secretary*

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DIVISION OF INDUSTRIAL AND ENGINEERING CHEMISTRY

The meeting of the Division was distinguished by two symposiums in addition to the general papers, and a special discussion of Mr. Midgley's paper. The first symposium was upon "Automatic Process Control," the chairman of which was L. W. Parsons.

The second symposium was upon "Combustion," and was under the auspices of the Division's new offspring, the Section of Gas and Fuel Chemistry, with R. T. Haslam as chairman. Without doubt it was the most interesting and instructive symposium of the meeting. Further details concerning this symposium are reported by the Section of Gas and Fuel Chemistry.

Thursday morning the Division discussed Midgley and Boyd's paper entitled "The Chemical Control of Gaseous Detonation with Particular Reference to the Internal-Combustion Engine." Keen interest in this subject was manifested and the discussion lasted nearly an hour. (See p. 894, this issue.)

The general papers covered nearly every phase of industrial chemistry. The grade of the papers was of a very high standard, and the frequent discussion showed that the authors were stimulating thought in their hearers.

The present active committees were continued.

The title of the symposium for the spring meeting at New Haven has not been decided upon as yet. "Agitation" has been suggested as a subject.

The attendance at the sessions of the Division was large. It reached as high as 350 and was considerably over 100 most of the time.

The following officers were elected:

Chairman: D. R. Sperry.
Vice Chairman: W. A. Peters, Jr.
Secretary: E. M. Billings.
Executive Committee: W. F. Hillebrand, Edward Mallinckrodt, Jr., F. M. De Beers, A. Silverman, H. R. Moody, C. E. Coates.

E. M. Billings, *Secretary*

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DIVISION OF LEATHER CHEMISTRY

The fourth meeting of this group had a program of 24 papers, all of which were read. In addition to the papers mentioned, a contribution was received from Dr. Edmund Stiasny, one of the most prominent leather chemists of continental Europe. The keynote of the program was the development of the fundamental principles of practical leather manufacture. Beginning with a series of papers on unhairing and bating, the entire processes of both chrome and vegetable tanning were covered. Explanations were given of the mechanism of the existing processes, together with the results of scientific investigations, leading to the development of new processes as well as the importance of the old ones. A feature of the program was the gelatin symposium in which the physical chemistry of gelatin was discussed. This symposium attracted a capacity audience. A paper by Dr. Jacques Loeb resulted in considerable discussion, in which Sheppard, Bogue, Davis, and Wilson participated.

The following officers were elected for the ensuing year:

Chairman: J. Arthur Wilson.
Vice Chairman: Charles S. Hollander.
Secretary: Arthur W. Thomas.
Executive Committee: F. P. Veitch, C. R. McKee.

Arthur W. Thomas, *Secretary*

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DIVISION OF ORGANIC CHEMISTRY

Of the 62 papers on the program, 57 were presented. Because of the length of the program, the presentation of papers was limited to 7 min. and the discussion of each paper to 3 min. The time limits were enforced with the aid of a "kodak timer." The actual time taken for the presentation of the papers and discussions was 8.5 hrs. The Division voted to continue the abstract service which had been inaugurated this year. The cost of this service for the two meetings was about $100 for 400 members. A committee was appointed to consider the necessity and desirability for changing the method of presenting papers. It was decided that it would be inadvisable to make any change at the present time. It was also decided to arrange a symposium on some suitable subjects for the New Haven meeting.

The officers elected for 1923 were:

Chairman. Frank C. Whitmore.
Secretary and Vice Chairman. R. R. Renshaw

Frank C. Whitmore, *Secretary*

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DIVISION OF PHYSICAL AND INORGANIC CHEMISTRY

The Division of Physical and Inorganic Chemistry held four sessions at which a very interesting program of 59 papers was presented.

After considerable discussion it was voted that the executive committee be instructed to consider and decide before the New Haven meeting as to the possibility of charging $1 or $1.50 dues and using the proceeds to send brief edited abstracts of all papers to all members in advance of the meeting. About 30 members signified their desire to be enrolled on this basis. All those desiring to have their names added to the list will please communicate with Secretary Graham Edgar, at the University of Virginia, Charlottesville, Va.

A committee was also appointed to canvass the Division for nominations for members of the board of editors of the new *Journal of Physical Chemistry*. After receipt of their detailed report, a list of names was recommended to the Advisory Committee of the Society.

The following officers were elected for the coming year:

Chairman: Robert E. Wilson.
Secretary: Graham Edgar.
Executive Committee. Farrington Daniels, G. H. Ellis, James Kendall, E. B. Millard, R. G. Van Name.

R. E. Wilson, *Secretary*

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DIVISION OF RUBBER CHEMISTRY

The Rubber Division had without doubt the most interesting meeting in its history. The attendance was never below 100 and often ran as high as 140. The outstanding features were the presentation of high-speed hysteresis data on rubber, by W. W. Vogt, and the partial disruption of our present theories of organic acceleration of vulcanization, by F. G. Breyer. Details of a machine and results obtained on various compounds were given by Mr. Vogt, which showed hysteresis losses in rubber when developing from 40 to 400 cycles per minute. This is approximately the number of cycles developed in an automobile tire running from 4 to 40 miles per hour. The results show variation from former data and throw light on the physical behavior of rubber in tires. Mr. Breyer presented considerable data on the relation of cure to particle size of compounding ingredients. We have heretofore considered zinc oxide incapable of acceleration, but attributed a good reinforcing effect in rubber to its use. Well-established data given by Mr. Breyer show that extremely fine zinc oxide is a fairly rapid accelerator, and when an ordinary organic accelerator is used in conjunction with it, the effect of the organic accelerator is merely to add tensile strength but not to shorten the cure. Interesting data on the structural reactions of organic accelerators were presented in different papers by Bedford, Scott, Gray, and Sebrell, as well as other valuable papers dealing with the influence of different ingredients in vulcanized rubber.

Committee work on research physical testing and standardization of chemical analysis is being continued, both committees presenting reports showing fine progress. A committee consisting of E. B. Spear, N. A. Shepard, D. F. Cranor, C. W. Sanderson, and H. V. Bloom was appointed to present standard testing formulas to the Division for consideration.

Officers were elected as follows:

Chairman: W. B. Wiegand.
Vce Chairman: E. B. Spear.
Secretary: Arnold H. Smith.
Executive Committee: C. W. Bedford, D. F. Cranor, G. S. Whitby, H. L. Fisher, N. A. Shepard.

Arnold H. Smith, *Secretary*

DIVISION OF SUGAR CHEMISTRY

In the absence of S. J. Osborn, who was detained by illness, the meeting was presided over by F. W. Zerban, vice chairman of the Division. The session as a whole was one of the best the Division has held. The attendance, while not as large as at some previous meetings, was good. The interest manifested in technological papers was greater than usual and foreshadows an increasing activity in the SOCIETY by the technical men of the industry. The program covered a wider range of subjects than usual.

Among the papers presented were a number of importance in precise analytical sugar work, the subject of reducing sugars being prominent. The subject of decolorizing carbons, recently of importance to the industry as a whole, was given considerable time and brought out much discussion. In addition, papers on bacteriology, factory operation, and laboratory apparatus were presented.

The following officers were elected for the coming year:

Chairman: W. D. HORNE.
Vice-Chairman: F. W. ZERBAN.
Secretary: FREDERICK BATES.
Executive Committee: W. B. NEWKIRK, C. E. COATES, C. A. BROWNE, S. J. OSBORN, H. E. ZITKOWSKI, H. S. PAYNE.

FREDERICK BATES, *Secretary*

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DIVISION OF WATER, SEWAGE, AND SANITATION

The varied and interesting program of the Division of Water, Sewage, and Sanitation was presented in full, each paper eliciting considerable comment. The paper, "Total and Available Calcium Hydroxide in Hydrated Lime," by A. S. Behrman and F. R. Porter, which introduced the special topic for discussion, namely, "Specifications for Lime for Water Treatment," was especially well received and developed a lively consideration of the whole subject of water softening. The report by Neave and Buswell, on the relative value of stirring *vs.* compressed air in the treatment of activated sludge, was of unusual interest and served as an introduction to a report, illustrated with photographs, by Dr. Bartow upon his observations during his recent European trip of the sewage treatment plants at Manchester, Sheffield, Bury, Strassburg, and Paris. An interesting report of some of the results of the inspection of commercial foreign and domestic waters, under the Federal Food and Drugs Act, was presented by Sale and Skinner.

The officers of the Division were reëlected for the ensuing year.

W. W. SKINNER, *Secretary*

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SECTION OF CHEMICAL EDUCATION

The Section of Chemical Education opened with an attendance of 241 at the first session. W. D. Bancroft, of Cornell University, presented the first paper on "Pandemic Chemistry." He stressed the great need for a course in chemistry intended for men who wish to learn something about the subject merely as a part of a general education, and briefly outlined such a course. He said that Cornell University is seriously considering starting a course on Pandemic Chemistry when the new laboratory is finished.

The next general topic of the "Correlation of High School and College Chemistry" was opened by L. W. Mattern, giving the high school standpoint, followed by another paper from the college's point of view by H. N. Holmes. Lyman C. Newell very keenly analyzed the entire forenoon's papers and discussions, and pointed out the difficulties that stand in the way of a proper correlation of high school and college chemistry. He believes that the two-course plan in college is the only fair one for students, and should be conducted when the class of beginners numbers 75 or more. Dr. Newell stated that the present basis of division into the two-course plan was not satisfactory, and suggested that teachers report at the New Haven meeting a new basis. It was voted that a committee of seven be appointed to study the proper correlation of high school and college chemistry and report their findings at the first meeting possible

The discussion of the afternoon centered around the general topic, "What Chemistry Shall Be Taught in Our Professional Schools?" L. B. Broughton cited the chemical requirements for premedical students as specified by the American Medical Association. W. F. Rudd, in discussing dental chemistry, touched upon the following points: first, the needs of freshmen students in chemistry in those dental schools requiring only high school graduation for matriculation; second, the needs in those schools requiring one year of college work for matriculation; third, the proper correlation of dental metallurgy and dental chemistry. J. C. Krantz described a method for the correlation of general and pharmaceutical chemistry, which received the applause of all present. C. W. Stoddart outlined an interesting course for agricultural chemistry which includes qualitative chemistry, agricultural chemistry including possibly organic chemistry and qualitative analysis, a separate course in organic chemistry, and a course in quantitative analysis which is closely allied with agricultural chemistry. C. W. Cuno discussed the present methods of teaching qualitative analysis as a preliminary to other courses in chemistry. Professors Gornoy and Bartow opened the Thursday morning program by a paper entitled "An Experience with the General Intelligence Tests in Teaching Freshman Chemistry." They showed how the general intelligence tests had a definite use in teaching freshmen chemistry, in spite of the fact that the marks of the student and the general intelligence ratings do not always have a close comparison. A motion was made and passed that a symposium on tests, including any standardizing test in chemistry, be held at the New Haven meeting.

A paper by B. T. Harvey, Jr., gave many helpful suggestions in meeting difficulties involved in teaching of chemistry in negro private schools. H. W. Moseley described a modified Hulett apparatus for the demonstration of the volumetric composition of water, and also a simple and effective ozonizer for lecture demonstration purposes. W. L. Estabrook gave a development of the Student's Laboratory Bench, including a demonstration of his apparatus. He also described two small wooden kits provided with shelves and capable of holding all the reagents, solids, and solutions needed in qualitative analysis, designed by L. J. Curtman of the College of the City of New York. R. A. Baker showed how the teaching of the electrochemical series might be of great aid in the teaching of chemistry. E. G. Mahin gave a clear idea of what he meant by the "Schoolmaster and the Teacher."

The Thursday afternoon session opened with Dr. Silverman acting as chairman. W. A. Noyes gave the first paper on "Proper Methods of Conducting Undergraduate Research." He said that if the instructor trained the student in proper methods of looking up chemical literature and developed personal initiative in the student, he had done much for the student's research career. R. E. Rose gave an extremely well worked out paper on "The Best College Course for the Chemist." His paper was such a radical departure from the course generally given to chemists that the Section did not seem to be ready to discuss it. This paper will undoubtedly be up for discussion at a later meeting when we will all have had time to read the article in full and think it through. J. B. Garner gave the last paper of the afternoon on "The Education of the Chemist." He showed in a very clear and convincing way that personality, mentality, and professional training are essential elements in the make-up of a chemist. Dr. Silverman made a motion that the Section of Chemical Education hold a joint meeting with the Division of Industrial and Engineering Chemistry, at which time there should be a symposium on industrial education. The motion was unanimously passed and the Milwaukee meeting was considered the best time for the symposium. The Section closed with the feeling that the next year holds much of value for all those interested in chemical education.

NEIL E. GORDON, *Secretary*

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MEETING OF ASSISTANT EDITORS AND ABSTRACTORS OF CHEMICAL ABSTRACTS

The abstractors' dinner and meeting was well attended, over forty being present. It was held at the Pittsburgh Bureau of Mines Cafeteria. The feature was a talk by the former editor, Austin M. Patterson, who emphasized the point that the abstractors and editors should feel that their work on the journal is just as important and dignified as any work which they do in their laboratories. Just as in the business world the old feeling is disappearing that those engaged in distribution are on a lower plane than those who are producers, so also in the field of science the attitude that the distributors serve a less important purpose than the producers, is passing.

Dr. Edward Bartow, who has just returned from Europe, reported favorable comments across the sea on the work of the abstractors of *Chemical Abstracts*.

E. J. CRANE

SECTION OF GAS AND FUEL CHEMISTRY

The initial meeting of the Section of Gas and Fuel Chemistry was a symposium on combustion held jointly with the Division of Industrial and Engineering Chemistry under the chairmanship of R. T. Haslam. The importance of efficiency in using our fuel supply was emphasized by the chairman, who pointed out that $2,500,000,000 per year is used at perhaps 10 per cent efficiency, so that even a small percentage increase in efficiency of combustion would represent a very great saving in dollars and cents.

Four of the papers in the symposium related to the physical-chemical principles underlying combustion reactions, developed from a semimathematical point of view. W. K. Lewis pointed out that the essential consideration is the burning of coke in the fuel bed where the velocity of various reactions occurring is of dominating importance. R. T. Haslam discussed two sets of reactions: (1) those occurring in simultaneous combustion of carbon monoxide and hydrogen; and (2) those in the production of water gas.

George F. Moulton reported on the extended investigations of that institution regarding domestic appliances designed for proper control of the combustion of gaseous fuels. A similar discussion of the problems involved in the burning of powdered coal was given from both a theoretical and practical point of view by Kreisinger and Blizard, who summarized the work done by the Bureau of Mines and the Combustion Engineering Corporation.

H. C. Dickinson described the important problems which demand consideration in a study of combustion in engine cylinders, pointing out the striking differences between reaction conditions there and in ordinary burners where gas or oil is burned at low pressure.

The final paper of the program was by J. A. Doyle on "Factors Governing the Selection of Fuels," with particular emphasis upon the importance of determining the cost per unit of the finished product, rather than simply theoretical efficiency or heating values.

Besides the symposium, 16 papers were presented at the meeting of this Section, and the large attendance and enthusiastic discussions prompted a vote of the Section requesting that the officers of the Society authorize a continuance of the session for the next general meeting. It is estimated that over 100 persons were present at the meetings of the Section, approximately 50 being in attendance continuously throughout the entire period.

The carbonization of coal was one of the most important general subjects considered. H. J. Rose described the new Becker coke oven, indicating the important increases in oven capacity which this new system of oven heating permits. The same author discussed the new electric method which has been developed for determining the by-product yields which can be expected from any coal.

A paper was given by H. J. Rose describing a system of impregnating the cut surface of a coke sample with a mixture of plaster of Paris and magnesia, in order to bring out the delicate detail of structure.

The methods of utilizing low-temperature cokes were discussed fully by H. A. Curtis, who described briefly the Carbocoal process for making low-temperature coke material which is then briquetted with pitch and made into a smokeless fuel which behaves much like anthracite and is entirely suitable for domestic use.

Physical-chemical studies of the forms of sulfur in coke indicate, according to A. R. Powell, that the sulfur exists both as a solid solution and as free sulfur physically adsorbed by the carbon, as well as in the form of ferrous sulfide.

The thermal efficiency of modern regenerative coke ovens was discussed by Wilson, Forrest, and Herty as a result of extended plant tests from which complete engineering data were obtained.

The constitution of coal and its relation to the storage of coal for combustion and the coking of coal was discussed in a series of five papers by S. W. Parr, T. E. Layng, and their associates in the University of Illinois. The same authors describe a method for determining the softening point of coal and the temperature at which the softened coal again solidifies as a coke.

Methods for the examination of low-temperature coal tars were reported on by J. J. Morgan and R. P. Soule. A paper by Weymouth, Anderson, and Fay described a new apparatus for determining specific gravity of gases in the field. The utilization of natural gas at low pressures for household work was discussed by Miss Anna P. Warren.

J. D. Davis described a new retort used for combustion of coal samples to determine directly available hydrogen. R. T. Haslam and L. Harris discussed the making of fuel producer gas from powdered coal in order to achieve higher over-all efficiencies from fuel used.

R. S. McBride, *Secretary*

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SECTION OF HISTORY OF CHEMISTRY

Chairman C. A. Browne in his introductory remarks described the exhibit of books on alchemy, medical chemistry, metallurgy, and also the autograph letters and documents. This exhibit of books included Agricola's "De Re Metallica," Emanuel Swedenborg's "Regnum Subterraneum," Sir John Pettus' "Fodinae Regales" (1670) and "Fleta Minor" (1683), and Albaro Alonso Barba's "Minerals and Metallurgy" (1726). Dr. Browne stated that a movement was already on foot to prepare a large and elaborate historical exhibit for the New Haven meeting.

President Edgar F. Smith, in his paper on "James Curtiss Booth, Chemist," called attention to the fact that he was one of the early presidents of the American Chemical Society. After giving a short account of Booth's student life at the University of Pennsylvania, he described in detail Booth's studies with Wöhler and Magnus. Upon his return to Philadelphia, Booth organized a student chemical laboratory which eventually became the well-known firm of Booth, Garrett & Blair, Analytical Chemists. Booth also contributed several important reports to the geology of Pennsylvania and Delaware. In fact, he made the first geological survey of Pennsylvania. His greatest contribution to chemistry was made during his service as Director of the Mint in Philadelphia, which position he held until his death. In fact, his death was hastened by the arduous labor connected with the development of the processes of refining California gold. Besides these three contributions to education and science, Booth prepared many reports for the Franklin Institute, translated a French chemistry, Regnault's book on chemistry, and also wrote an encyclopedia of chemistry.

In his second paper, President Smith gave a vivid account of the chemical work of Richard Watson, the Bishop of Llandaff, and exhibited his portrait and autographed letter and a volume of his essays. John A. Mathews described in detail the development of iron-making in the colonies from the first iron made from iron ore in Jamestown in 1608 until just after the American Revolution. In his paper on "Some Relations of Early Chemistry in America to Medicine," Dr. Browne described the work of John Winthrop, Jr., George Stockey, and William Beaumont. F. B. Dains, in "The Early History of Some Experiments in General Chemistry," showed that many of the experiments performed are really very old. The cartoons of van't Hoff shown by Ralph H. McKee epitomized the career of van't Hoff in a pleasing manner. Elton R. Darling pointed out that bromine was produced in Pennsylvania and other states many years ago and the flourishing industry was established long before the present one in Michigan. Lyman C. Newell's letters of Davy emphasized the striking characteristics of the famous English chemist, and the two diplomas signed by Dalton brought vividly to the audience the contributions of this English chemist to the atomic theory. The unpublished letter of Berzelius interpreted by Anton R. Rose revealed the versatility of the great Swedish chemist.

The officers of the Section were reappointed and are making arrangements for the New Haven meeting.

Lyman C. Newell, *Secretary*

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SECTION OF PETROLEUM CHEMISTRY

The meeting of the Petroleum Section, the fourth since its organization at Rochester, was marked by a large attendance, the steady interest of technologists prominent and influential in the petroleum industry, and a noticeable awakening of attention from chemists identified with the theoretical, rather than the applied science. A great deal of interest attached to the activities of the Section in promoting research on petroleum, and the matter was discussed thoroughly. The committee appointed at Birmingham to select a list of problems for immediate attack and to coöperate with the Research Division of the American Petroleum Institute reported, and was instructed to consider at once means for starting work on the research problems on a coöperative basis. It is hoped that, besides the direct benefit resulting from the solution of the problems attacked, this activity of the Section will result in awakening the interest of chemists generally in the field of petroleum chemistry.

The program included some fourteen papers of general interest, a symposium on "Lubrication from the Chemists' Viewpoint," and a discussion on the origin of petroleum. The latter consisted of formal papers by R. E. Somers and R. Thiessen, and discussion by C. F. Mabery and W. H. Emig. The papers in the lubrication symposium covered the chemical composition of lubricants, the mathematical aspects of lubrication, and some practical questions. Unfortunately, several of these papers remained unread because of the absence of the authors. There was much open discussion.

The change from the sectional to the divisional form of organization was authorized at this meeting. The officers elected under this authority were:

Chairman: T. G. Delbridge.
Vice Chairman: R. R. Matthews.
Secretary: W. A. Gruse.
Executive Committee: E. W. Dean, W. F. Faragher.

W. A. Gruse, *Secretary*

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CHAIRMEN AND SECRETARIES GROUP

About 35 chairmen and secretaries met at three o'clock Thursday afternoon. In the absence of W. Lee Lewis, E. C. Franklin of Leland Stanford University presided.

Since the term of office of Professor Lewis had expired, it was in order to elect a presiding officer for the coming year. Professor Lewis was unanimously reëlected.

The Secretary read a letter of Professor Lewis relative to the activities of the group. The results of the questionnaires sent to the different Sections were reported. After discussing both sides of the question whether or not it would be advisable to ask the national officers to give this group the status of "Section" it was unanimously voted to make this request.

Much valuable discussion took place with regard to the best method of securing members for the Society, how to get members acquainted, and how to get local publicity. The itinerary of the speaking tour of E. C. Franklin was laid out. The following Sections are planning to have him speak before their members at the time he comes east for the spring meeting at New Haven: Chicago, Detroit, East Lansing, University of Michigan, Purdue, Cleveland, New Orleans, West Virginia, Pittsburgh, Buffalo, Rochester, Syracuse, and Philadelphia. It is hoped that other Sections will also attempt to have Dr. Franklin on their programs while he is on his way to the meeting.

Dr. Miner of the Chicago Section told of a typical program before the Chicago Section. The meeting was divided into four parts, and at the close of the discussions before these groups the members came together and enjoyed sandwiches and a social time.

It was suggested that the Chairmen and Secretaries Group get together for an informal discussion at each national meeting, owing to the decided change in personnel, and also to the fact that different sections of the country were visited.

It was also pointed out that much interest was stimulated in Sections by holding joint meetings with their neighbors, and it was planned to have at least one intersectional meeting a year. This brings about good fellowship and gives the younger men in the Sections a chance to present papers and become acquainted with the leaders in the chemical profession.

Erle M. Billings, *Secretary*

American Ceramic Society Summer Excursion Meeting, August 13 to 19, 1922

This meeting was purely an excursion. There were no literary or executive sessions held, the entire occasion being devoted to plant inspection and to meeting with the several people in the different localities.

The trip down the St. Lawrence to Montreal is well worth the while of any one who desires to observe scenery, architecture, or human nature. One could not possibly talk shop on such a trip.

The reception accorded by the officials of the potteries and glass companies in Montreal was most cordial. They entertained the seventy-five guests Monday evening with a smoker, and on Tu[illegible]

Tuesday was filled with plant and city visitations. The McGill University with its several laboratories and museums was visited by practically every delegate. The Montreal potteries, glass companies, brick works, and enameling works entertained them royally.

On Wednesday the party journeyed to Buckingham to visit the feldspar mines of O'Brien and Fowler. They were met in Buckingham by automobiles for a ten-mile ride into the wilds. Here they saw the quarrying of feldspar under the most modern conditions and by the most modern methods. A wonderful camp dinner was served and the delegates were entertained with singing by local talent.

From Buckingham the party continued in special cars to Ottawa, where a banquet was served and the Victoria National Museum and the Department of Mines were visited.

On Thursday afternoon the party divided into groups and visited different ceramic plants, paper mills, and other points of interest in the city.

The party left the city at 10:40 for Verona, where again they were royally received and entertained, and motored up into the mountains to the Richardson feldspar deposit, after which they continued their journey to Kingston where they were received by the Kingston Council.

The cordial reception given, the banquets served, the addresses made by distinguished Canadians repaid the delegates for the time and expense of the trip. Words cannot express the appreciation of the wonderful service rendered by the Canadian Pacific Railway. The party had the same parlor cars and porters from Montreal around to Kingston, and the continuous service thus afforded made the trip easy. After the banquet Thursday night in Kingston, the party took special sleepers for Toronto, finding that while they were at the banquet their bags had been conveyed from the special parlor cars to the sleepers by representatives of the Canadian Pacific Railway. This is typical of the sort of service that Canada gave the American delegates.

At Toronto the party was received with the same cordiality, and the day's stay was planned with the same detail and expedited in the same fashion as on the other days. In Toronto and on the next day in Hamilton the party saw more of the works that were branches of American companies. Sanitary works, glass works of all sorts, brick and tile companies, universities and museums afforded a wide variety of interesting and instructive things to be seen.

The American Ceramic Society would fail in its real purpose if it did not afford its members these opportunities for excursions, not only to see ceramic plants, but to see the best that nature affords in lakes, rivers, mountains, etc., and also the best products of human effort, not only in the universities, museums, wonderful cities, but also in mankind. This trip on Lake Ontario, down the St. Lawrence, and up into the Canadian mountains, completely encircling Lake Ontario cannot be surpassed in the large variety and quality of things to be seen, entertainment furnished and in opportunities for studying and observing manufacturing. [Ross C. Purdy, *General Secretary*.]

Meeting of Chemical Equipment Association

The Chemical Equipment Association, at its final organization meeting on September 2, 1922, at which 32 active and 4 associate members were present, elected the following officers:

President: Pierce D. Schenck, Duriron Co.
Vice Presidents: Walter A. Lummis, Adolph Coors, Jr., Coors Co., George J. Lehman, Bethlehem Foundry Co.
Treasurer: P. C. Kingsbury, General Ceramics Co.
Directors: H. N. Spicer, Dorr Co.; J. I. Lyle, Carrier Co.; P. S. Barnes, Pfaudler Co.; Edw. C. Alford, Shriver Co.; T. C. Oliver, Chemical Construction Co.; H. H. Alport, E. B. Badger Co.

This association was organized on May 10, 1922, for the purpose of fostering trade in chemical process equipment. The aims of this association are given on page 564 of the June issue of This Journal.

Chemical Salesmen Meet

The Salesmen's Association of the American Chemical Industry, in executive session at the Hotel Commodore, New York, on September 12, 1922, elected the following officers for the next year:

President: John W. Boyer, The Mathieson Alkali Works, Inc.
Vice Presidents: F. M. Fargo, Jr., Calco Chemical Co.; Edward Van Berlo, Wilckes-Martin-Wilckes Co.; Edgar M. Queeny, Monsanto Chemical Works.
Secretaries: J. D. Lowery, Kalbfleisch Corp.; George T. Short, Wilckes-Martin-Wilckes Co.
Executive Committee: Williams Haynes, Drug & Chemical Markets; R. T. Dunning, The Barrett Co.; W. S. Goff, Monsanto Chemical Works.

NOTES AND CORRESPONDENCE

A Criticism of the Technical Press

Editor of the Journal of Industrial and Engineering Chemistry:

A shortcoming of the chemical press of to-day is the lack of forceful, constructive criticism of the profession. The technical journals ably expound to the layman the value, achievements, and necessity of chemical control and research in industry, and in this we must admit they do a great service to the chemist. But this is only a part of their duty. They should clearly and persistently point out to the chemist his own weaknesses and the pitfalls that surround him. To trust this self-analysis to the individual chemist is asking too much of human nature. We are none of us prone to search out our faults, but it is wholesome and necessary that they be pointed out to us.

You have in your JOURNAL an interesting and valuable department—"The Earning Power of Research." I would suggest another department under some such title as "Business Mistakes of Chemists," frankly devoted to picking apart and criticizing the activities of the average chemist in industry, which should have a cumulative effect in maintaining high standards of effectiveness in the profession.

Another duty of the technical magazine is education. The average chemist is unaware that his education is incomplete in the details of business. The chemical laboratory, whether research or testing, presents in miniature all the administrative and executive problems of the industrial plant. Its raw materials are reagents and chemicals, its finished product, service or information. All the industrial problems are met here, whether the force consists of two or thirty—buying, storage and control of raw materials, securing, training, and development of competent workers, upkeep of equipment, maintenance of quality, and quantity of production. The problems of merchandizing also enter in. Is the product of the highest attainable quality, and does it meet in an adequate way the customer's special needs (the "customer" being of course the firm, department, or man making use of the results)? Is it properly presented and explained? Viewed in this light, the operation of a laboratory at its greatest efficiency for commercial purposes, requires, besides mastery of the principles and technic of the science involved, application of the basic principles of economics and psychology, business instinct, and attention to business detail. Chemists do not study and apply as extensively as they might the excellent works available in efficiency and business management. It would be to their advantage to do so, for the man who really can, and knows he can, make every dollar invested produce the maximum result in any line of endeavor is never without a job. Further, he is the type of man most justified in going into business for himself. The technical magazine should call attention to books on these subjects, publish articles dealing with the application of sound economic principles to the chemist's daily work, and investigate and endorse, or even institute, if necessary, suitable correspondence courses for instruction in these subjects.

The technical journal can render a further service in the cultivation of morale. The chemist is perhaps a little too ready to bewail his lot when things do not suit him, and instead of being discouraged in this attitude by the technical press, he is led to feel that his services are not appreciated. Granting some basis of truth in this, it is surely not a healthy viewpoint to adopt, nor one that can lead to real progress. The technical journal can be of assistance here by trying to inculcate a forward-looking viewpoint which makes light of difficulties and brings success in its wake. This is no time for the chemist to repine. The present era of close competition, which will probably last for a period of years, is his golden opportunity to prove his worth as a money saver and money maker. But, like everyone else, he must be prepared to work harder than before.

The captious may comment that seemingly all that is further necessary to bring the technical journal up to date is the adoption of a pretty-girl cover, a woman's page, and a bed-time story, but I sincerely believe that the chemist in industry will look more and more to the technical press for guidance and inspiration as well as for technical information. The time is past when a mere bound file of proceedings and technical reports and papers will fully serve his needs.

I believe that a technical journal working strongly along these or similar lines would in a few years exert an enormous influence for the better on the morale, efficiency, and prosperity of the chemical profession.

HUGO V. HANSEN

45 NORTH SPRING ST.
BLOOMFIELD, N. J.
June 15, 1922

The Continuous Countercurrent Lixiviation of Charred Kelp

Editor of the Journal of Industrial and Engineering Chemistry:

The article on "The Continuous Countercurrent Lixiviation of Charred Kelp," by J. W. Turrentine and P. S. Shoaff, in THIS JOURNAL, **14** (1921), 605, offers excellent opportunity for application of the theory of discontinuous extraction developed in THIS JOURNAL, **9** (1917), 866. The data given in the article, together with other figures on the water content in the filter cakes—kindly furnished by the authors—make it possible to compare the ratio of KCl to water in the solutions with those in the corresponding filter cakes. In Filter Cake 1 the ratio of KCl to water was 37.6 to 100, while in Brine 1, supposed to have been in equilibrium with the filter cake, the ratio was only 30.2 to 100, showing that there was some undissolved KCl in the first filter cake, or, what is just as bad, the solution remaining in the cake was of higher concentration than that removed by filtration. In the same way it was found that the ratio of KCl to water in Filter Cake 2 was 10.6 to 100 and in Brine 2, 10 to 100, showing that the solution was not quite complete even after the second treatment. By the theory of discontinuous extraction, undissolved solute after the first treatment decreases the efficiency of the process, and this process could, therefore, have been improved by better mixing or higher temperature in Agitator 1.

This note is not offered as adverse criticism of Turrentine's process, but simply as an example of a method of studying discontinuous extraction processes to determine where improvement can be made. In this particular process the solvent ratios are so high and the general efficiency so good that these considerable quantities of KCl undissolved after the first treatment probably do not affect the recovery by more than a few tenths of a per cent, but in many processes such undissolved solute might seriously decrease the recoveries.

It would be inadvisable to finish this note without explaining why a discontinuous extraction theory is applied to a process called continuous. The explanation is that the process is really a typical discontinuous, countercurrent extraction, but instead of taking the space to prove this assertion we will leave it as a problem for those of your readers who are interested in the theory of extraction. Here is a paradox. In an extraction process the raw materials enter and the finished products leave the system continuously, and all the intermediate products are constantly in motion, and yet the process is *dis*continuous, countercurrent extraction.

L. F. HAWLEY, *In Charge*
Section of Derived Products

FOREST PRODUCTS LABORATORY
MADISON, WISCONSIN
July 27, 1922

Editor of the Journal of Industrial and Engineering Chemistry:

With reference to the communication of Dr. L. F. Hawley, permit me to say that when a process in which the raw materials are being added continuously, the intermediate products are in motion continuously, the extraction up to the point where equilibrium exists between solid and solvent takes place continuously, the finished products are discharged continuously, and which is in practical operation continuously, is yet *dis*continuous, it might be contended that the definition is more open to criticism than the process.

J. W. TURRENTINE

EXPERIMENTAL KELP POTASH PLANT
SUMMERLAND, CALIFORNIA

Larger Quantities of Creatine Available

Editor of the Journal of Industrial and Engineering Chemistry:

It should interest biological and pharmaceutical chemists to learn that creatine, heretofore obtainable only in gram lots at a price of several dollars a gram, is now available in much larger quantities. A source of this material has been discovered which, while not unlimited, is capable of yielding at least some hundreds of pounds of pure creatine a year.

In order that research workers may be able to benefit by this discovery, a considerable quantity of pure creatine has been prepared, and will shortly be available through regular supply houses at a fraction of one per cent of its present price.

It is hoped that this new source of creatine may aid materially in extending our knowledge of this and related substances, as the quantity now available should permit research in this field along the lines of nutrition, pharmacy, and synthetic organic chemistry, as well as biochemistry, without exorbitant expense.

The writer will be glad to give further details to anyone interested.

GRAHAM EDGAR

UNIVERSITY OF VIRGINIA
UNIVERSITY, VA.
August [illegible] 1922

Correction

On page 745 of the August issue of THIS JOURNAL, change the heading "Society of Chemical Industry Reports" to read "Chemical Society (London) Reports." Also make the following change in the first line of the text: Delete the words "Society of Chemical Industry" and substitute "Chemical Society (London)," making that portion of the sentence read: "The Council of the Chemical Society (London) is prepared to offer, etc."

Chemists Storm the Capitol

Editor of the Journal of Industrial and Engineering Chemistry:

On August 16, 1922, twenty-six research, operating, and analytical chemists,[1] representing sixteen different synthetic organic chemical plants, mustered up courage enough to present without other support their side of the embargo question to the arbiters of the tariff at Washington. "A horde" Senator Moses called us on the floor of the Senate. I presume, however, we should be grateful for even that public recognition—it is one of the few that chemists, as such, have had.

Sunday, August 13, the outlook for the embargo seemed particularly black. Since its failure would mean to the country the irreparable loss of the industry and to us the equally serious loss of our jobs, Messrs. Orelup, Schepmoes, and myself, in discussing the matter on that day, concluded that we had little to lose and everything to gain by organizing a group of men similarly situated to present the chemists' side of the organic chemical tariff in Washington.

The time was too short for long explanations, but we felt certain the cause was so good that but few men would be unwilling to risk the relatively small cost of the trip in the hope of doing something to save their industry and positions. All honor to those men who joined us, but we were sadly discouraged in a great number of cases. Some who would not join us felt that the chemists would not know enough about the situation to be effective, or would be ignored. Fancy! After long years of arduous training and an average of several years of practical experience, we are still uncertain of our abilities to meet men and present our ideas! As for being ignored, it is a rare public representative indeed that desires to avoid his constituency, much less dares to!

As a matter of fact, we had not only an interesting and instructive visit, but we most certainly aided in the accomplishment of our ends. Senator Frelinghuysen graciously aided us in arranging interviews with the President, Secretary Hoover, and with the other members of the Senate Finance Committee. We interviewed Senators Edge, McCumber, McLean, Watson, Calder, Lenroot, Sterling, Shortridge, Capper, Fletcher, Sheppard, Nicholson, McCormick, and Borah, and quite evidently influenced several former embargo opponents in favor of the Bursum Amendment than pending.

At least partly as a result of our plea, Senator Ransdell not only voted for the Bursum Amendment but also made a speech in favor of it. Probably the most interesting result of our visit was the outcome of our long talk with Senator Borah, who promised a vote in favor of an embargo to be long enough to reëstablish the industry, if our contention proved true—that two months of the then tariff (without the Bursum Amendment) would put us out of business.

One thing our visit made plain—that legislation is accomplished by far different means than research along chemical lines. From our talk with one senator it was quite plain that uncorrected misstatements had been made on the floor about our industry, and that the actual situation was little appreciated except among those already favorable to the measure. It was obvious that, not only was it not undesirable for such a party of individuals to press its case, but that it would be absolutely fatal not to, for without "lobbying" of a sort proper legislation could not be obtained.

Finally, I hope that some of your readers will send to the *Con-*

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[1] The members of the party were: A. P. Beardsley, James Brown, E. E. Hartmann, J. J. Johnson, P. V. Rosenvelt, H. A. Van Brocklin, L. L. Perry, J. W. Orelup, F. A. Novotny, R. W. Feder, C. H. Schepmoes, W. W. Weck, William Goldstein, W. A. Lucas, L. M. Shafer, N. R. Viera, C. Hamilton Merrill, R. E. B. Richards, C. A. Swan, E. G. Parker, A. C. Wintringham, W. H. Van Winkle, M. T. Coakley, T. B. Clendenning, and L. C. Ohlsson.

gressional Record Office, The Capitol, Washington, for copies (at about 10 cents each) of that very interesting publication of August 17 and 18, where on pages 12,537 and 12,576 will be found the debate on the Bursum Amendment. Let them not fail to read the words of Senator Moses on page 12,542: "I suppose, Mr. President, the way to become a chemist in this country is to put a label in your lapel." Then let them ponder how far the chemist in this country has yet to go to find his place in the sun, and how much personal effort each must put forth to do it.

A. J. PASTENE

CHEMICAL COMPANY OF AMERICA
SPRINGFIELD, N. J.
August 25, 1922

Canadian Letter

By T. Lindsay Crossley

208 KING ST., WEST, TORONTO, CANADA

Canadian industries using heavy chemicals are buying in larger quantities, and while this business has not by a large margin reached the volume hoped for, the improvement in the last five months has been marked.

Canada seems to be popular as a summer meeting place. These visitors are not only welcome, but they are an inspiration to good fellowship. Last month we had the Chemical Engineers and the Leather Chemists. Ere this appears, the American Ceramic Society will have been with us, and the American Electrochemical Society will visit Montreal and Shawinigan, September 21 to 23.

They will see one of our best examples of industrial development in the St. Maurice Valley, due to the magnificent water powers of the St. Maurice River at Shawinigan and Grand Mere, developing about 225,000 h. p. at both places, with a third power of about the same amount, not developed, at Les Gres below Shawinigan. Grand Mere is a pulp, paper, and power town controlled by the Laurentide Company. Shawinigan has pulp and paper mills, carbide, electrometallurgical and aluminium works, foundry, cotton mills, and technical school. Here was developed the biological process for acetic acid, and here were made special aluminium alloys for aeroplane construction, and the first commercial magnesium in America.

The Canadian Institute of Chemistry is planning an active program for the fall and winter, and is rapidly becoming a factor in the scientific development of the country.

It is said that one reason for the lack of public attention to the work of chemists is that chemists themselves do not coöperate and are not found mingling with the folks in the market place. With a view to meeting this criticism in some small measure, the chemists of Toronto have inaugurated an informal luncheon club, meeting every Monday at the Engineers' Club, where questions of general interest are discussed and from time to time action by various organizations may be suggested. This has already been found of practical value.

Some discussion has been aroused by a proposal made during the Ottawa convention to adopt the word "chemor" as applying to consulting, analytical, or engineering chemists, to avoid the confusion arising from the idea, perhaps more prevalent in British communities, that chemist is synonymous with retail druggist. In fact, some provincial legislation in Canada makes the pharmacist the only person legally defined as a *chemist*. Hence the suggested new appellation to bring the distinction to public notice.

August 2, 1922

The Plant Manager and the Chemist

Editor of the Journal of Industrial and Engineering Chemistry:

I cannot allow Mr. George L. O'Brien's criticisms of the chemist in THIS JOURNAL, **14** (1922), 650, to pass unanswered.

Chemists, like other people, are neither perfect nor infallible and their ideas are not always practicable, neither are those of any manager I have known.

Mr. O'Brien would make of the chemist the "catalytic agent" or go-between of about everything that transpires in the plant and community, yet without authority. If it were possible to fill such a position, I can scarcely see what occasion there would be for a manager. A man of such parts would be discredited for holding a subordinate position.

It is as important for a manager to know management as it is for a chemist to know chemistry. Believe me, I have seen some managers who were out of place. Chemists, with slight exceptions, are conscientious workers, but in the business of management I have seen many examples of a betrayal of trust.

Often there has been, and is yet, a lack of coöperation between the management and the chemist. The manager does not know how to make the best use of his chemist and he is often suspicious of the man who has new and original ideas. The time is rapidly approaching when the chemical industry will be managed by chemical engineers, as it should be.

I have one important criticism to make of the manager. Generally speaking, he expects to pay a chemist a clerk's salary, and too often, I regret to say, he gets away with it because the chemist is willing to take a position which he is led to believe promises a "future." A chemist is always at a disadvantage in looking for a position. It is not a popular profession and not many chemists are wanted.

Chemistry lies at the foundation of all life and being, and its pursuit requires special natural qualifications, consistent, hard, and conscientious endeavor. The chemist is not above criticism but he should be dealt with in a kindly sympathetic spirit of encouragement. Mr. O'Brien concludes his criticism with a very high compliment to the chemist when he says, "much of the progress of civilization rests with him," and that, "his activities are of such great importance that modern industrial manufacture without his help is unthinkable."

MARTIN L. GRIFFIN, *Chemist*

MT. HOPE FINISHING COMPANY
NORTH DIGHTON, MASS.
July 29, 1922

Figures Talk

The registration, by states, of those present at the Pittsburgh meeting of the A. C. S. was as follows:

Alabama	1	Maine	3	Oregon	1
Arkansas	2	Maryland	30	Pennsylvania	582
California	4	Massachusetts	47	Rhode Island	1
Colorado	3	Michigan	25	Tennessee	2
Connecticut	14	Minnesota	10	Texas	4
Delaware	16	Mississippi	3	Utah	1
		Missouri	11	Vermont	2
District of Columbia	62	Nebraska	2	Virginia	10
Georgia	2	New Hampshire	2	Washington	2
Illinois	69	New Jersey	38	West Virginia	21
Indiana	20	New Mexico	1	Wisconsin	25
Iowa	11	New York	150	Canada	6
Kansas	5	North Dakota	1	England	2
Kentucky	2	Ohio	159	Cuba	2
Louisiana	7	Oklahoma	1		

TOTAL REGISTRATION 1362

Studies of the effects of sulfides on animals are being made at the Bureau of Mines Experiment Station, Pittsburgh, Pa., by a number of consulting physiologists, including Yandell Henderson, Howard W. Haggard, C. W. Mitchell, and W. P. Yant.

LONDON LETTER

By Hugh Griffiths, 15 New Bridge St., London, E. C. 4, England

Crystallizing Plants

Considerable interest is now being taken in this country in the modern types of apparatus for crystallization in motion; a number of firms having installed new plants during the past few months. In view of the recent decision under the Key Industries Bill in connection with sodium hyposulfite, it is probable that much more attention will have to be paid to the form and appearance of commercial chemicals. Sodium hyposulfite of "photographic quality" is now scheduled, and while it was clearly stated by the Referee that "pea-crystal hypo" may not be of "photographic quality," the latter term is taken to indicate a product of good color and high purity in the form of small uniform crystals.

While this may be considered a clear definition, it will be recognized that most photographers have their own ideas as to what photographic quality "hypo" looks like, and usually they will expect to receive either the "cube crystal" or "pea-crystal" form. Like many other users of chemicals, they do not usually make an analysis of materials but judge of their suitability from appearance. The photographer's experience has led him to associate satisfactory performance with a certain appearance, and it is therefore necessary for the manufacturer to meet his ideas.

The same considerations apply to every chemical product to some extent, and it is safe to say that a crystalline substance of regular appearance consisting of individual grains of uniform size and shape is generally more readily salable than the less beautiful ordinary qualities. This is not necessarily the result of fad, but is because the user has learned that a carefully crystallized material will generally be better in other respects also.

A large number of inorganic substances are now sold in regular crystalline form, all these having the same essential features, namely, the crystals being approximately of pea size or larger, and the crystals being quite separate and not formed in groups, and each being of nearly perfect shape and of uniform size.

The production of these qualities on a large scale is generally only possible in special plants, only the fine grain materials being produced in ordinary agitator-crystallizers and stationary vessels yielding agglomerated masses of crystals.

At present, two types of plant are being used: a simple open plant, and a more elaborate vacuum apparatus. The open plant consists essentially of a long trough of approximately elliptical section which is oscillated on roller bearings by means of gearing. This trough has no jacket, the cooling being for the most part due to the evaporation of water from the exposed liquor. These machines are generally between 30 and 80 ft. in length.

The solution to be crystallized is run into this trough at one end, and the small crystals which are at first formed gradually increase in size as they pass on a zigzag path through the apparatus; the finished crystals together with the mother liquor are discharged at the other end and received on suitable draining apparatus. The motion of the crystals in the trough prevents agglomeration, and if the correct physical conditions are chosen, most inorganic commercial salts can be turned out from these simple machines in the form of regular individuals of even size. Quite apart from any question of appearance and quality of products, these machines are proving attractive on account of the continuity of operation and economy of labor.

Some modifications have been introduced into these plants recently in order to secure better control over the crystal size, but details are not yet available for publication.

The vacuum crystallizers are also of the oscillating type, and consist of cylindrical boilers supported on rollers, the various connections being made through hollow trunnion packings. These may be of any size, and while they are more elaborate than the open crystallizers, their application appears to be more generally possible and the crystals may be produced in very large sizes. The writer has some samples of cane sugar crystallized in these machines, and the crystals are about $1^1/_2$ in. across, weigh about 1 oz. each, and are perfectly shaped and separate individuals just like crystallographic models.

It is to be expected that the study of the operation of these plants will lead to a better knowledge of the *rationale* of crystallization. Most chemists find it difficult to believe that large crystals can be obtained from a moving liquor, but it is now well established that if the other conditions are correct and the formation of too many new centers of crystallization can be avoided, perfect crystals can only be produced from a liquid in motion. The convection currents in ordinary stationary crystallizers seem to have been forgotten.

The two types of plant mentioned above are now in use on many different materials: sodium sulfate, sulfite, thiosulfate, sulfide, phosphate, nitrate, carbonate, alums, chlorate, bichromate, copper sulfate, sugar, organic acids, etc.

Nitric Acid Manufacture

The latest volume of the "Technical Records of Explosives Supply," on the manufacture of nitric acid from nitrate of soda, gives a fairly accurate account of the present state of English practice.

While silica-coil condensation systems are favored in many quarters, the preponderance of technical opinion is certainly in favor of the Hart plant, in which condensation is effected mainly in glass tubes about $1^1/_4$ in. diameter. As in America, the systems employing submerged condensers are not recommended, owing to the serious consequences of a leakage of water into the condenser—namely, the dilution of an entire batch of acid, which is expensive to concentrate.

The speeds of distillation given in the report are for war practice, and under ordinary conditions most works are content to make two runs from each plant per 24 hrs., and with gas-fired retorts this speed can be maintained comfortably while securing a very high over-all efficiency.

The use of silicon-iron condensing plants is not common in England, owing to the difficulty in obtaining really sound castings in such alloys. Some years before the war a system very similar to that described in the August issue was given a very thorough trial, the only essential difference being that the S-pipes were of flattened section. Such systems have been tried repeatedly since that time, but invariably they have been given up, owing to the difficulty experienced in getting pipes free from blow-holes and graphite pockets. Some of the makers of acid-resisting castings are now adding a small proportion of nickel with a view to securing a finer grained metal, and are also taking steps to produce clean sound castings. One manufacturer has succeeded in producing straight tubes in this metal by the centrifugal process, and the solution to the difficulty may be found in this method. There is, of course, no question that, given really good castings, the silicon-iron condenser would be far better than any ceramic production.

The report gives some particulars of an interesting attempt to construct a continuously working plant for reconcentration of nitric acid, by running the mixture of nitric and sulfuric acids through a packed tower heated externally by producer gas. Several continuous systems for this concentration have been tried in England, but none of them have been found to be so satisfactory as the simple distillation process, repair charges generally proving to be excessive.

Methyl Bromide

While ethyl chloride, methyl chloride, and ethyl bromide are all inflammable, it has been pointed out by Albert Henning that methyl bromide is not only noninflammable but a very powerful fire extinguisher, and patents have been taken out to cover application of this material as a solvent, as a refrigerating agent, and also as a fire extinguisher.

It is specially interesting as a fire extinguisher, as, by reason of its low boiling point, 4° C., it does not require mechanical devices for projection, the vapor pressure being adequate to propel the bromide from a suitable container fitted with a simple nozzle. Such extinguishers have been demonstrated on several occasions recently, and it has also been shown that petrol is rendered noninflammable by admixture with about one-fifth the proportion of methyl bromide as compared with carbon tetrachloride. This is not surprising in view of the vapor pressures of these materials. It is also claimed that there is less danger of poisoning than with tetrachloride.

For refrigerating purposes both methyl bromide and mixtures of methyl bromide and ethyl chloride are now in use in place of ethyl chloride in the small size machines. The fire risk, which has always been the most serious objection to these machines, is therefore eliminated.

August 26, 1922.

PARIS LETTER

By Charles Lormand, 4 Avenue de l'Observatoire, Paris, France

The Dye Industry

The syndicate of dyestuff consumers has taken the initiative in asking for customs regulations to protect this industry, but limiting this protection to dyes made in France. The dyestuffs not yet made in French factories would be almost entirely free from duty.

This measure seems to be rather tardy, for the production of dyes in France is increasing daily. The French importation of dyes before the war reached 95 per cent of the national consumption. In 1920 the amount of imports was not more than 60 per cent; in 1921 and at the beginning of 1922 it decreased to 20 per cent. In 1920, 50 per cent of the amount imported came from Germany (3000 out of 6000 tons); in 1921 the importation was only 400 tons, coming from Germany.

This decrease of importation is due largely to the efforts of the National Company of Dyestuffs and Chemical Products. I mentioned previously the rumor concerning the union of this company with the German companies. This rumor has been, and is still, contradicted. Nevertheless, the dye company has bought a number of patents from the foreigners. It certainly does not wish to lose time in perfecting the manufacture of intermediate products; it has resolutely acquired all the manufacturing processes that it has been able to find concerning these products.

The procedure of selling dyestuffs by chemical engineers specializing in dyestuffs is being developed in France. This method of selling the manufactured products has been successful; it gives satisfaction to weavers and dyers by permitting collaboration with technical color chemists. These technicians have themselves made the chemicals in special laboratories where the uses of coloring materials are studied.

Measurement of Weak Radioactivities

The electroscopes now used for measuring weak radioactivities are all derived, more or less, from the electroscope of Curie and Laborde. Mr. Szilard has proposed a spiral electroscope. The needle is movable and the index rigid, and is electrically joined to the case. It is attracted by an insulated dial and charged by a very small electric friction machine. The needle is suspended by a fine ribbon stretched so that the torsion will be an antagonistic couple.

With such an electroscope, Mr. Szilard has been able to measure on 500 g. of a product containing 10^{-9} of radium per gram. One division of his apparatus corresponds to 10^{-4} electrostatic units, which is to say a content of 0.001 U_3O_8. This apparatus seems destined to render great service in the measurement of weak radioactivity control of manufacture in radium factories, prospecting of minerals, examination of fertilizers and medicines with weak radioactivity.

The Nitrogen Problem

The French Parliament was dismissed before making a decision on this question. This is especially unfortunate, as we are still in a period of discussion between the two processes—Haber and Claude. It is a national fault of ours to spend much time in discussions after making an interesting discovery, so that we are too late to put it into use.

Mr. Matignon at Marseilles gave us information as to the nitrogen situation in Germany. In this country there has been a slight increase in price of nitrogen products, due to an increase in cost of transportation.

In spite of last year's catastrophe, the factory at Oppau has since February 1922 returned to its normal production, which is 100,000 tons of pure nitrogen per year. The factories at Leuna are producing 200,000 tons per year. The dividends issued by the different societies of chemical industries (Hoechst, Badische, etc.) have increased about one-third.

Furthermore, Germany has made herself completely independent of the nitrates from Chile, of which she received 750,000 tons before the war. She imported from Chile in 1921 only 35,000 tons of nitrates, which have been replaced by calcium nitrate. The Bavarian factories are furnishing 80,000 tons of this per year, the Saxony plants, 175,000 tons. These plants use the Franck-Caro process.

By summing up the different quantities of nitrogen produced in Germany, both as nitrates and as ammonia, it can be seen that at the present time Germany produces about three times as much as it can consume for its agricultural needs. With a low rate of exchange it can rapidly become an exporter of this product, while we in France are still in a period of discussion.

Our investigators, however, are continuing their study of the different phases of the problem, and Mr. Sabatier has just specified the conditions of obtaining urea directly from carbonic acid and ammonia. On the other hand, Mr. Matignon has also fixed the conditions of obtaining ammonium sulfate directly by treating calcium sulfate (gypsum) with ammonium carbonate. At ordinary temperatures by agitation for 2 or 3 hrs. with gypsum a concentrated solution of ammonium carbonate changes into a solution of ammonium sulfate. This conversion is almost total, as the coefficient of conversion is 96 per cent.

International Council of Research

The International Council of Research has just convened at Brussels. Around this International Council are now grouped five great international Unions: Astronomy, Geodesy and Geophysics, Mathematics, Scientific Radiotelegraphy, Pure and Applied Chemistry. Only the Union of Pure and Applied Chemistry meets annually.

Four new Unions have been established: Pure and Applied Physics, Biological Sciences, Medical Sciences, Geography.

The decline of the German mark has made possible at the Stassfurt mines a large exportation of their potash, and just as the Dyestuffs Company has had to form an alliance with the German societies, the companies mining Alsatian potash have had to seek an alliance with the German producers. Preliminary arrangements have been under way since May. They have been difficult to bring about, but they seem now to be nearly completed.

The impossibility of bringing about payment by Germany is going to cause more and more French industries to seek special alliances with industries on the other side of the Rhine. It is well understood that these alliances are purely economic and not political, and that they leave to the French industry all complete freedom of action.

The English society, British Dyestuffs Corporation, has in the last few years undergone great financial difficulties. The factories which it has erected, constructed hastily, perhaps with insufficient technical preparation, have not been able to furnish the same quality of dyestuffs as those furnished by the German or Swiss concerns. The English customers, have, therefore, finally returned to these old suppliers. In spite of the tariff duties protecting the British Dyestuffs Corporation, this society was in danger and engaged in conferences with the president of the syndicate of German producers of dyestuffs. No agreement was made, because of the fact that the English society did not succeed in making acceptable to the German representatives the principle of absolute autonomy of the English dyestuffs industry corresponding to the needs of peace time as well as to those of war. The French Dyestuff Company has been able to come to the agreement of which I have spoken. Now, in France, we only import 15 per cent of our total consumption of dyestuffs.

The International Congress of Geology has just been held at Brussels. One of the questions which they have been discussing with much breadth is that of sources of petroleum. A specialist in this matter, Mr. Voitesti, of the University of Cluj (Roumania) has examined the sources of petroleum in the Transylvanian region. Mr. Bogdanovitch showed the parallelism of bituminous and petroleum deposits with the richness in phosphates of neighboring rocks. The author came to this conclusion following the discovery of bituminous and phosphate schist in the state of Montana, U. S. A.

From October 9 to 15 there will take place in Paris the International Congress of Combustible Liquids, presided over by Prof. Sabatier, a member of the Institute. This Congress is divided into six sections: (1) Petroleum, (2) Schists, (3) Coals and Peats, (4) Tars and Benzol, (5) Alcohols, and (6) Vegetable Oils.

September 1, 1922

JAPAN LETTER

By K. Kashima, 1125 Ikebukuro, near Tokyo, Japan

The fixation of atmospheric nitrogen is an important problem in European countries and also in Japan. Under the jurisdiction of the Agricultural and Commercial Department, an institute, Special Research Laboratory for Nitrogen, was established in 1917 at Meguro, near Tokyo, to study this problem and its application to industry. Dr. Fusakichi Odera, formerly research chemist of the Tokyo Industrial Laboratory, was placed in charge of the laboratory. Details of the progress of the institute have not yet been published. Three reports have, however, appeared: concentration of nitric acid using sulfuric acid as a condensing agent; a general review of the fixation of atmospheric nitrogen; and the electrolysis of cyanamide, its salts, and dicyandiamide in aqueous solutions.

The same problem is now under consideration by the Institute of Chemical and Physical Research, and also by some fertilizer companies. Two companies were founded by the Mitsui and Mitsubishi, with plants in Kyushu, and employ the cyanamide process. Suzuki and Company, in Kobe, have recently purchased the apparatus and patent for the fixation of nitrogen from Georges Claude of France. This apparatus is also protected by the Japanese patent law. Founded on this and other patents, the Nitrogenous Industrial Company of the Claude System is being organized with a capital of 15,000,000 yen to manufacture ammonia, ammonium sulfate, and other derivatives.

The fuel situation is another international problem. Recently, two institutes have been established to study this question: The Research Laboratory of the Naval Fuel Department at Tokuyama in Yamaguchi Prefecture; and the Fuel Laboratory, of which Mr. Manji Yoshimura is in charge. The latter, which is under the control of the Agricultural and Commercial Department, will study general fuel problems and their industrial application. The former, under the Naval Department, will conduct research work on fuels for ships.

During the past year, Tatsuzo Hatori of Minami-hirayanagi-nura, near Kawaguchi-machi in Saitama Prefecture, made the startling announcement that by heating certain common substances in a crucible with suitable reagents, he had succeeded in isolating some small silver grains. These substances did not reveal the presence of silver by the methods ordinarily employed. His announcement aroused the interest of chemists, many of whom called upon him and examined his work. But they could not explain his findings. Some thought them fantastic. The inventor himself has not been able to offer a scientific explanation. He is not a college man but is a trained technician. Dr. Tsuneya Marusawa, professor of applied chemistry in the Kyushu Imperial University, and Dr. Sadahiko Sato are greatly interested in his work and are conducting investigations with a view to finding the scientific explanation for this discovery. Dr. Sato has recently announced that he can isolate silver from some substances which do not yield silver by the usual analytical method, but has not yet advanced a scientific explanation.

July 15, 1922

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Books and journals published in the United States and European countries are frequently bound with metallic wires. They are not, however, suitable for Japan, owing to the great humidity. Japan is a wet country, the humidity being at a minimum in January, about 60 per cent, and at a maximum in July, about 90 per cent. Metallic wires used for binding books and journals, leathers used for covering cameras and other purposes, and many wooden articles are apt to be destroyed during June to August.

Many patents for waterproof paper or cloth have been taken out. Prof. K. Ikeda has perfected a process for the manufacture of drying agents. As material, Japanese acid clay (fuller's earth) was selected, which is being largely used as decolorizing material of mineral, vegetable, and animal oils. The clay is compressed to a prism 10 to 15 mm. long and a sectional area of about 4 sq. mm., and heated to a high temperature. By passing moist air or other gases through a layer of the prism, it is easily dried. By the decrease of 1 mm. of the vapor tension, the temperature of the gas is raised by 2°. When the absorbing power of the clay is lost, it is reactivated by heating or by passing heated air.

A. Maire, chief engineer of St. Médard powder-mill, has visited this country and is now delivering lectures on chemistry and technology concerning explosives, etc. The visit of American chemists is very much welcomed. It would be a great pleasure if we could hear their opinions directly. It has already been announced that Prof. Einstein will visit this country next autumn and deliver some lectures on his great theory. If visitors drop into our laboratory, every assistance in our power will be gladly offered.

Research is the life of scientific men in the laboratory, but it consumes money. The funds for research in universities, technical and other schools are not plenty. For a few years, the Educational Department has been granting some money (about 1000 to 3000 yen per problem) to scientific men in universities, technical, higher, or medical schools, etc. This year, about 30 professors were appointed for such research. Works achieved by this fund are now being published in general chemical journals or special memoirs of each school.

There have been three chemical journals written by Japanese—*Journal of the Chemical Society of Japan*, formerly *Journal of the Tokyo Chemical Society*, founded in 1880, *Journal of Chemical Industry*, founded in 1898, and *Journal of the Pharmaceutical Society of Japan*, founded in 1882. This year two new chemical journals have been published, *Acta Phytochimica*, edited by Prof. K. Shibata, and *The Journal of Biochemistry*, edited by Prof. S. Kakiuchi. They contain articles written in English, French, and German.

The National Research Council of Japan has also published this year one proceedings and eight journals—on astronomy and geophysics, chemistry, physics, geology and geography, botany, zoölogy, medical science, and engineering. They contain transactions written in English, French, and German, and abstracts written in English of articles published in Japan. Besides these, we have one chemical news (semimonthly), two rather popular chemical journals, and many special publications from institutes, colleges, or laboratories.

An institute for studying metallic materials was newly established in the Tôhoku Imperial University in Sendai instead of the Iron and Steel Laboratory, Prof. K. Honda being appointed as the director of the Institute. A chair for biochemistry has been established in the Kyoto Imperial University and is held by Prof. S. Komatsu. It will also be created in the Tokyo Imperial University in the near future.

August 11, 1922

A Uniform Working Temperature

For some time the need for uniform alcohol tables and a uniform temperature for making routine observations has been felt. There has been some criticism of the two standards now in most common use, that of the A. O. A. C., which is based on the Bureau of Standards table 20°/4°, and that of the U. S. P., based on the Bureau of Standards tables 15.56°/15.56°. In order to obtain a consensus of opinion as to preferences, the following questionnaire was recently sent out to members of the A. O. A. C.:

1—Are you in favor of the A. O A. C. alcohol tables?

2—Are you in favor of the U. S. P., 9th Revision, alcohol tables?

3—What single working temperature do you consider best for determining specific gravities, optical readings, refractive indices, immersion refractometer readings, etc.?

Of the replies received, the vast majority voting favor the A. O. A. C. tables, and 20° as the best temperature for making determinations.

In order to get a larger and more representative vote, it has been suggested that others, who are interested in establishing uniform tables and temperature for making observations, send their vote on the three questions, especially on the question of uniform, general working temperature. The preferences of the members of the AMERICAN CHEMICAL SOCIETY are especially desired in this matter. Suggestions should be sent to L. F. Kebler, *Chairman*, A. O. A. C. Committee on Pharmacopeial Revision, Bureau of Chemistry, Washington, D. C.

WASHINGTON NOTES

DYE SITUATION

On August 17, 1922, just about a month after the dye embargo was defeated by a vote of 32 to 38, the Senate, by vote of 38 to 23, adopted the Bursum Amendment, which increased the duty on coal-tar intermediates from 50 per cent ad valorem and 7 cents per lb. foreign valuation to 75 per cent ad valorem and $10^{1}/_{2}$ cents per lb. American valuation. It also increased the duty on coal-tar chemicals and dyes from 60 per cent ad valorem and 7 cents per lb. foreign valuation to 90 per cent ad valorem and $10^{1}/_{2}$ cents per lb. American valuation. It further empowered the President, after thorough investigation, to make certain reductions in these schedules.

When the conferees reached this item in their consideration of the Tariff Bill, they rejected the Bursum Amendment and substituted the dye embargo. Then the House took its turn and, after an acrid debate of several hours, by a vote of 177 to 130, recommitted the bill to the conferees with instructions to abandon the embargo and to place potash on the free list. It is believed that it was this linking of the dye embargo with potash that caused the defeat of both in the House. The conferees agreed to the action taken in the House, but with the proviso that the new rates adopted should be based upon American valuation.

And now, as we go to press, another step has been taken toward the restoration of the dye embargo. On September 16, Senator Wadsworth introduced a Joint Resolution in the Senate, providing that the embargo be extended for four months after the passage of the Tariff Bill. On the following day Representative Tilson introduced a similar resolution in the House, except that under the terms of the House Resolution the embargo is to be retained for three months instead of four. Coincident with this action, Secretary Mellon called attention to the difficulty that will be experienced by customs officials in determining American values, and suggested that time be allowed these officers to determine the American values on dyes imported into this country.

The dye industry is having a hard fight, but it seems incredible that a way will not be found to insure the adequate protection of this industry.

HELIUM PLANT REOPENED

A large plant for the extraction of helium from natural gas has been reopened at Fort Worth, Texas. The appropriations made by Congress for this work are sufficient to permit the plant to operate for practically the entire year. It is under the general supervision of the Navy and is operated by the Linde Company under a government contract. The plant has been shut down since November 1, 1921.

DYE PRODUCTION IN 1921

A report of the United States Tariff Commission states that on account of the loss of export trade, business depression, and large stocks on hand, the dye production in this country showed a marked decline as compared with the previous year. However, notwithstanding poor business conditions, a considerable number of complex dyes were developed and introduced during the year. Many of these dyes are essential to special processes of dyeing and printing, although the quantity consumed makes them of secondary importance from that standpoint. The development of these new products is a notable technical achievement and represents further progress toward rounding out our coal-tar chemical industry.

There were 201 firms manufacturing coal-tar derivatives in 1921. The output of dyes by 74 of these firms was something more than 39,000,000 lbs., representing a decrease of 56 per cent from the 1920 production. The sales during the same period were more than 47,000,000 lbs., with a value exceeding $39,000,000. Sales exceeded production by 22 per cent, indicating clearly the presence of large stocks carried over from the previous year's abnormally high production. The sales for 1921 exceeded the imports of 1914, when nearly 46,000,000 lbs. were imported and 6,000,000 lbs. of dyes made from German imported intermediates.

It is worth noting that the average price of all dyes in 1921 was 83 cents per lb., compared with a value of $1.08 per lb. in 1920 and $1.26 for 1917. The importations were 3,914,036 lbs. valued at $1.32 per lb., making a total of $5,155,779, compared with $5,763,437 for 3,402,582 lbs. the previous year. Of the dyes imported, Germany supplied about 48 per cent, Switzerland 41 per cent, England 7 per cent, and other countries 4 per cent.

Exports of American dyes for 1921 decreased nearly 79 per cent as compared with 1920. They were less than for the year 1917 when the vast expansion of domestic dye industries from those of pre-war times occurred.

The development of the synthetic organic chemical industry has been similar to that of the dye industry, and the production of medicinals, perfumes, flavoring ingredients, and solvents is 21,545,186 lbs.

GOVERNMENT EMPLOYEES

The following statistics taken from data issued by the Civil Service Commission show the changes in the number of government employees which are wholly or principally the result of the World War:

	Employees in District of Columbia June 30, 1922	Employees Outside District of Columbia June 30, 1922
State	595	3,257
Treasury	19,860	36,110
War	4,921	46,358
Navy	7,377	48,470
Labor	1,161	2,364
Shipping Board[1]	1,888	2,182
Railroad Administration	1,123	124
Alien Property Custodian	139	....
Supt., State, W. & N. Bldgs	1,006	....
Veterans' Bureau	5,321	26,481
Railroad Labor Board	....	75
Civil Service Commission	379	30
TOTALS	43,770	165,451

[1] Include administrative offices of Emergency Fleet Corporation, but not workmen at yards or employees in warehouses or on vessels.

SUMMARY

NUMBER OF EMPLOYEES	In District of Columbia	Outside District of Columbia	TOTAL
June 30, 1916	39,442	398,615	438,057
June 30, 1922	69,980	490,883	560,863
INCREASE, ENTIRE SERVICE	30,538	92,268	122,806

THE SURGEON GENERAL DESIRES COÖPERATION ON THE PART OF INDUSTRY

As part of a comprehensive study under the direction of the Assistant Secretary of War, the Medical Department of the Army is undertaking a study of the sources from which the supplies which it uses can be obtained. The Medical Department is not only concerned with the provision of the personnel necessary to the treatment of the sick, but is also charged with the supply of those things that are required by such personnel.

The armamentarium of modern medicine is exceedingly intricate, but without it the wonderful advances made in medicine are not available to the sick and injured, however skilful the personnel. The difficulties encountered in providing such elaborate equipment in time of war for the large number of new hospitals, infirmaries and first aid stations necessary, and particularly in providing it at these institutions in the advance area, are manifest, and yet, if the soldier is to be given the service that he is entitled to, it must be provided.

In a war of any magnitude the burden thrown upon industry for the production of these supplies is enormous. Any information that could be made available in advance to industry as to type, number, and quality, would obviously be of great advantage to industry in its plans. The Surgeon General, therefore, side by side with his plans for the extension of the Officers' Reserve Corps, with his plans for instructing medical students through the R. O. T. C. in those duties of a medical officer which differ from those of the civilian physician, is determining where the supplies needed by these officers may be had, should any grave emergency arise.

This effort is an attempt to do beforehand what was necessary after the declaration of war in the recent World War. It is in recognition of the fact that the forces of the Medical Department, however numerous and skilful they may be, will be but half prepared without the necessary equipment. In brief, the program contemplates: (1) That a careful determination shall be made, not only of the items needed, but of the quantity thereof. If a close liaison with industry is established, it is probable that final decision as to the type of an article selected will be determined often by the facilities of industry to produce it in large quantity; (2) the plan contemplates also a roster of personnel skilled in the manufacture, and the inspection and purchase of the various commodity groups. It is desired to secure from industry itself men who are eligible and will accept reserve corps commissions with a view to their assignment in time of emergency to the procurement of the commodity in which they are specialists. It is purposed that upon these men reliance will be placed in time of peace for advice and assistance in the study of industrial facilities, and that in time of war they will be assigned to the centers of industry or to Washington for procurement duty; (3) the plan further contemplates that a thorough study be made of the facilities of the country to produce the essential and important items of the supply table, and to have on file in the office of the Surgeon General such reports as will enable the immediate placing of contracts in the event of any national emergency.

In this work the Surgeon General realizes that he must rely upon industry itself, and it is hoped to secure definite and complete information from the manufacturers as to the aid they can render. It is probable that in an emergency of any magnitude Congress would again establish control of raw materials, labor, transportation, and installations; and the medical department expects that, with such information on file, it will be in a position to render great assistance to the firms making medical department supplies. It can prevent the drafting of skilled labor, the taking of key men, can assure the supply of material, of coal, and of transportation, and thus obviate difficulties in the operation of the plant.

At the direction of Secretary Fall of the Interior Department, T. E. Swigart, petroleum technologist, and C. E. Beecher, oil recovery engineer, of the Bureau of Mines, have been designated to compile a handbook of conservation methods in petroleum production, to be used by operators on leased public lands. The manual will include discussions of sources of wastes in oil and gas fields; suggested methods of preventing wastes in the production of oil and gas; and a complete, revised set of rules, regulations, and penalties for violation of regulations as applied to oil and gas production on public lands of the United States.

The Carbohydrate Laboratory of the Bureau of Chemistry has developed a cheap, effective, and rapid process for preparing chocolate creams having very soft cream centers. Invertase, instead of an acid, has been used to secure the semiliquefaction of the centers, the flavor developed being superior to that ordinarily secured by other methods. Application has been made for a public service patent to cover this process.

September 18, 1922

OBITUARY

Dr. Jokichi Takamine

ONLY to a few men is the opportunity given to act as so strong a link between two nations as was Jokichi Takamine, who died in Lenox Hill Hospital, New York, N. Y., on July 22, 1922, at the age of 67, after an illness of many months. His earnest desire for lasting friendship and good understanding between his native land of Japan and his adopted home of America was continually evidenced in his manifold activities.

Jokichi Takamine

Dr. Takamine was born November 3, 1854, in Takaoka, Japan, his father being physician to the Prince of Kaga. At the age of twelve he was sent to Nagasaki to study under the tutelage of the Portuguese consul, and later went to Osaka to study medicine. He became more interested in chemistry than in medicine, and entering the Imperial University at Tokyo graduated as a chemical engineer in 1879. The government then sent him to Great Britain for three years' special study in the University of Glasgow and Andersonian University. Upon his return to Japan he was appointed chief chemist of the Department of Agriculture and Commerce. His work in this capacity did much to improve the brewing industry of Japan and led to his lifelong activity in the scientific investigation and commercial development of diastatic ferments. In 1884 he came as representative of the Japanese government to the Cotton Centennial Exposition at New Orleans. Here he met Miss Caroline Hitch, whom he married in 1885. He planned to make his home in the United States, but returned to Tokyo in 1887 to erect there the first superphosphate plant in Japan. In 1890, he again came to America, and not long thereafter, as the result of his researches upon diastatic ferments, organized the Takamine Ferment Company in Chicago. These same researches resulted in the development of Takadiastase for medicinal use.

In [illegible] of crystallized adrenalin as the active principle of the suprarenal glands brought to a climax a long series of researches by various eminent men, and made its commercial production possible. It is in this connection that the name of Takamine is most widely known.

He was instrumental in the establishment in Japan of numerous chemical industries, including the production of alkali, aluminium, fertilizers, and dyes, and also formed there a large pharmaceutical corporation, Sankyo and Company.

In recognition of his accomplishments the University of Tokyo in 1899 bestowed on him the degree of Doctor of Chemical Engineering, and in 1906 that of Doctor of Pharmacology. His ability was so highly esteemed by his native country that in 1913 the Emperor appointed him a member of the Royal Academy of Science and in 1915 decorated him with the Fourth Order of the Rising Sun.

Dr. Takamine's industrial interests were many, including the presidency of Sankyo and Company of Tokyo, the Takamine Ferment Co., the International Takamine Ferment Co., and Takamine Laboratories, Inc. He was also a consulting chemist for Parke, Davis and Company.

His scientific and social relationships were equally numerous. He was a member of the American Chemical Society, The Chemical Society of England, the Institute of Chemical Engineers, and the Franklin Institute, as well as one of the founders of The Chemical and Physical Research Society of Japan. Besides holding membership in many New York clubs, he was chiefly instrumental in founding the Nippon Club of New York and the Japan-America Society, and was among the founders of the Japan Club and the Japanese Association of New York.

Those who knew him personally will remember him best for his kindliness, his thoughtfulness of others, and his intense devotion to every duty he deemed to be his.

His industrial ability achieved commercial success for himself and others; his scientific attainments brought him deserved honors; but a no less important contribution to the world's welfare was the years of quiet and persistent endeavor to promote enduring friendship between two great peoples; to interpret to each other the nations of his birth and his adoption.

Frank O. Taylor

Personals

Mr. Robert I. Wray and **Mr. Fulton B. Flick** have accepted positions in the Research Bureau of the Aluminum Company of America, New Kensington, Pa.

Mr. John W. Crombie is now research associate at the American Sheet & Tin Plate Research Laboratory, Pittsburgh, Pa.

Mr. Donald E. Cable has resigned as assistant research chemist in the Agricultural Experiment Station of the University of Wyoming and has been awarded a university fellowship in chemical engineering at Columbia University.

On July 31, **Dr. H. D. Gibbs** resigned his connection as research chemist with E. I. du Pont de Nemours & Co., Wilmington, Del., and will take a much-needed vacation. For the present his address will be c/o Chemists' Club, New York, N. Y., or c/o Cosmos Club, Washington, D. C.

On July 1, **A. A. Holmes** resigned from the staff of E. B. Badger & Sons Co., Boston, Mass., to accept the sales managership for the Trona Corporation. His headquarters will be in the Woolworth Building, New York, N. Y.

Dr. James Kendall has been promoted to a full professorship at Columbia University. He is to begin his sabbatical leave of absence next February, and has arranged to divide his time between Stanford University and the University of California.

Mr. H. Gardner McKerrow, who for the past three years has been advertising manager for the National Aniline & Chemical Co., Inc., has resigned and will engage in business in New York, as an advertising and merchandizing consultant, specializing in textile and chemical matters.

Mr. M. B. Crowe has severed his connections with the Crown Oil & Refining Company and has accepted a position in the Acid Recovery Department of the United Lead Co., Houston, Texas.

Mr. Ulric J. Lebourveau, Stamford, Conn., has resigned from the Atlas Powder Co., where he was engaged in experimental development work.

Dr. Gerald L. Wendt resigned on July 1 as associate professor of chemistry at the University of Chicago to join the staff of the Standard Oil Company of Indiana in the direction of research.

Mr. Leslie H. Webb, vice president of the Wedge Mechanical Furnace Co., is now in charge of the Pittsburgh office of the Pennsylvania Salt Mfg. Co., of which the Wedge Company is a subsidiary.

At a recent meeting the State Board of Regents changed the form of administration of the graduate work of the University of North Dakota from that of a department in charge of a graduate committee to that of a graduate school, and **Dr. G. A. Abbott,** head of the chemistry department, was appointed dean of the graduate school.

Dr. H. C. Trimble, associate professor of organic and physiological chemistry in the University of North Dakota, has been granted leave of absence in order to pursue special studies with Dr. Folin of Harvard.

Mr. Washington Platt has resigned his position as production manager of the Harris Laboratories to become associated with the Merrell-Soule Sales Corporation of Syracuse, N. Y., as manager of the Technical Service Department.

Mr. F. W. Barker, Jr., has resigned from the National Aniline & Chemical Co., Inc., and has become associated with The Kaumagraph Co., New York, N. Y.

Prof. Robert E. Wilson has left the Massachusetts Institute of Technology, where he was director of the Research Laboratory of Applied Chemistry, to assume direction of research for the Standard Oil Company at Whiting, Indiana.

Dr. J. A. LeClerc has severed his connections as chief chemist with the Miner-Hillard Milling Company and has assumed his duties as Special Agent in the Department of Commerce, Washington, D. C.

Dr. T. T. Read, chief of the Information Service of the U. S. Bureau of Mines, was appointed official representative of the American Institute of Mining and Metallurgical Engineers to attend the International Congress of Engineering held in Rio de Janeiro, Brazil, in September.

The Trustees of Columbia University have granted **Victor K. LaMer,** instructor in chemistry, leave of absence for the year 1922–23 to accept the Wm. Bayard Cutting Traveling Fellowship. Dr. LaMer sailed about September 15 for England and Denmark, where he will continue his studies in physical chemistry.

Industrials

On July 26, 1922, the new laboratories of the Research Association of British Rubber & Tire Manufacturers at Croyden, England, were formally opened. The association was formed in 1919 for the study of the fundamental problems of the rubber industry, the preparation of information dealing with control of manufacturing operations, the testing of raw materials and final products for practical use, the collection of rubber literature, the adjudication of scientific disputes, and the coördination of scientific and technical work in national emergencies. Some practical work in the study of physical and chemical problems has been carried on in laboratories at University College, London, but with the opening of the new laboratories it is expected that the full program will soon be put into execution.

As a direct result of the amalgamation of the General Bakelite Co., the Condensite Company of America, and the Redmanol Chemical Products Co., the Electroplax Company has been established at Toronto. The company is being financed entirely by Canadian money, and will produce the cold molded products and the various industrial articles now made by all the companies in the United States. The officers of the new company are: president and general manager, H. E. Corey; vice president, L. V. Redman; manager, W. M. Davidson; factory superintendent, J. B. Rathbun; chemist, W. A. Campbell.

Celite Products Limited has been established in Canada to market Sil-O-Cel and Filter-Cel as produced by the Celite Company in the United States. Sil-O-Cel is used for the prevention of excessive heat loss from boilers, furnaces, etc., while Filter-Cel is used in filtering to secure greater clarity and brilliance of filtrate. Mr. Lawrence Russel has been appointed Canadian manager, with offices in the New Birks Building, Montreal.

Brotherton & Company Ltd., Leeds, England, have published a booklet entitled "Hydros" which gives in some detail the method employed by them in the quantitative determination of sodium hydrosulfite.

Jayne & Sidebottom, Inc., New York City, have been appointed by the Darco Sales Corporation as sole selling agents in the New York metropolitan district and New Jersey for Darco decolorizing carbons.

The Salt Lake Insecticide Co., Salt Lake, Utah, has begun work on its plant for manufacturing calcium arsenate from the Scorodite ore found in the Gold Hill district, Utah. The arsenic ore is said to be high grade and is located in a hill of limestone-granodiorite. Dr. Frank K. Cameron discovered the process by which the ore can be economically treated and manufactured into calcium arsenate, and will act as general manager of the plant.

The Westmoreland Chemical & Color Co., Philadelphia, Pa., has had its plant closed as a public nuisance by order of the director of the Health Department. For several years there have been complaints that the escape of sulfuric acid fumes has caused considerable damage to property and the health of the residents in that section of the city, but until recently the company has been able to have definite action deferred on the plea that it was working on a special washer that would enable it to recover the acid. The present order requires that the plant shall remain closed until a system shall have been installed that will effectually prevent the escape of the acid fumes.

The Cellulose Products Co., incorporated under the laws of Delaware for the purpose of manufacturing artificial straw and hair, is to have a modern brick and steel factory building erected for it by the Chamber of Commerce of Milford, Del. It is said that this plant will be the first of its kind in America.

The following statistics are given relative to the exports from and imports into the United States of dyes during June 1922:

Exports

VEGETABLE DYE EXTRACTS	LBS.
Logwood extract	366,871
Other dye extracts	286,554
COAL-TAR COLORS, ETC.	
Color lakes	282
Other colors, dyes, and stains	398,975

Imports

	LBS.
Alizarin and alizarin dyes	71,887
Colors or dyes	292,676
Indigo, synthetic	8,310
Extracts and decoctions for dyeing	323,239

BOOK REVIEWS

Der Betriebs-Chemiker. Ein Hilfsbuch für die Praxis des Chemischen Fabrikbetriebes. By Dr. Richard Dierbach, [illegible] and Dr. Ing. Bruno Waeser, Chemiker. 3rd edition. x + 334 pp., 117 illustrations. Julius Springer, Berlin, 1921.

An examination of this excellent publication awakens a sense of the need for a similar handbook in English, adapted to conditions prevailing in industrial chemical plants on this continent. This is exactly the book for the young chemist or chemical engineer finding his place in the operating organization of a chemical industry for the first time. It gives a vast fund of detailed information concerning those important details which most textbooks sublimely ignore. The availability of such a book in English would undoubtedly eliminate the asking of many questions, and would prevent many foolish mistakes in setting up chemical plant of all kind.

The book is conveniently divided into sections, the first of which constitutes the bulk of the book. This section is divided into chapters on materials of construction, piping, valves, meters, furnaces, boilers, engines and electrical power transmission, material handling, and pumping equipment. The second section deals with the location and construction of buildings; the third, with the functions of the industrial chemist, and the maintenance of laboratories; the fourth, with safety engineering; and the fifth is a sort of symposium of short papers on various manufacturing operations, grinding, mixing, evaporating, distilling, drying, etc. Unfortunately, the authors have felt it necessary to limit themselves to very few pages on each of these subjects, and the information given is hardly full enough to be of any real help and the material is probably included here merely for the sake of completeness. The sixth section gives a very brief treatment of by-products; the seventh deals with chemical plant accounting, but merely skims the surface of this involved subject; and the eighth deals with packing and shipping.

The book is well printed and the illustrations are excellent. The binding, however, is not particularly well adapted to the hard service which such a book must receive.

F. M. Turner, Jr.

Power Alcohol: Its Production and Utilization. By G. W. Monier-Williams, O.B.E., M.C., M.A., Ph.D. 323 pp. Henry Froude and Hodder & Stoughton, London, 1922. Price, 21s. net

This book appears at a time when it is most needed. Alcohol will unquestionably be one of the ingredients of the future motor fuel. The author should be commended for his efforts to help at this critical time and congratulated on his able presentation of the subject.

The motor fuel problem is clearly defined in the first chapter; more stress should be laid, however, on the possible development of the steam engine for motor purposes.

Three-fifths of the book is given over to the manufacture of alcohol. This is as it should be. The chapters on fermentation are clear, though technical. Perhaps a better appreciation of the conditions in the United States and of the importance of molasses would improve the treatise as an international text. The addition of more engineering detail would have increased the value of the book. This is especially true of the chapter on distillation.

Dr. Monier-Williams has analyzed the situation without stating his personal conclusions, leaving the reader to form his own opinions which could be done more quickly if the author had summarized his data.

The remaining two-fifths of the book deals with denaturation, the internal combustion engine, properties of alcohol, fuel tests, and fuel mixtures. The importance of the denaturant is well brought out. The chapters on the internal combustion engine, and on properties of alcohol, are concise and clearly stated. The chapter covering motor fuel tests is an excellent review of the reliable work that has been done, but a one-page summary of the results would aid the reader in obtaining a clearer perspective. The final chapter describing fuel mixtures deserves more space because of its present interest.

The author states that alcohol is not going to become immediately a competitor of gasoline but a mixture containing alcohol will soon become a substitute for gasoline. He does not state, however, that gasoline must be one of the components of this mixture, an opinion that is held by many.

"Power Alcohol" is of particular importance to the English reader, but the American will find it both interesting and valuable

D. B. Keyes

Kolloide Lösungen. By Joachim Leimdörfer. 107 pp. Verlag für Chem. Industrie, H. Ziolkowsky, G. m. b. H. Augsburg, Germany, 1921. Price, M. 65 +.

The author, who is well known for his work on soaps, takes great pains to give colloids their proper perspective and his book (whose preface dated August 1914 indicates a long delay in its publication) possesses a somewhat philosophical character.

Starting with three essentials: (1) material movable particles (matter); (2) motion (energy); and (3) space, he points out that the three ideal states of the aggregation of matter—gas, liquid and solid—may coexist. From the work of von Weimarn and O. Lehmann, the author concludes that aggregation is the consequence of the vectorial orientation of matter, and he terms "crystal atoms" small material units whose sizes run between those of atoms and those of biological cells, and whose combination may yield macroscopic crystals or develop to cellular size.

Condensing matter gives off energy to the surrounding "solvent," and may yield coarse mechanical subdivisions, colloidal dispersions, or chemical combinations. In true solutions the forces are balanced, but colloidal solutions, possessing residual potential energy, are labile. Chemical combinations are broadly distinguished from dispersions in that the units involved are of a definite size, which persists under fixed conditions.

The book is deficient in experimental matter, but gives a general review of the subject based mainly on the work of Thomas Graham, Wo. Ostwald, P. P. von Weimarn, and others. During the seven years that the manuscript lay dormant, great strides have been made, and it will be interesting to see how the author will react in a new edition, when he becomes acquainted with the more recent work of American and British physicists and chemists, *i. e.*, of Thompson, Rutherford, Aston and Moseley, W. C. McC. Lewis, H. R. Procter and J. A. Wilson, of Milliken, Langmuir, Harkins, and G. N. Lewis, of T. W. Richards, J. Loeb, M. H. Fischer, and many others. His views will also be modified by the results of Scherrer at Göttingen with Bragg's X-ray spectrometer, which showed that colloidal solutions (*i. e.*, of SiO_2 and SnO_2) may contain both crystalline and amorphous or haphazard molecular clusters, whereas gelatin showed no crystalline groups.

Jerome Alexander

The Manufacture of Pulp and Paper by the Joint Committee on Vocational Education. Vol. 3. Joint Committee on Vocational Education representing the Pulp and Paper Industry of the United States and Canada. McGraw-Hill Book Co., Inc., New York, 1922. Price, $5.00.

This volume by nine experienced men contains a very full account of this subject to date, and the appliances and processes are very well illustrated. In general, the authors have not been as conscious of their audiences (students) as they should have been. Descriptive matter has been given more prominence than underlying principles, through which alone progress is made. There is considerable overlapping and repetition.

Somewhere in the complete book a discussion of the power plant, water supply, and transportation in the manufacturing processes should have been covered. As a work of reference a more complete bibliography should have been included.

The book commends itself as the product of practical men rather than book-makers. The committee and the associations they represent deserve only praise for undertaking such a task designed to enlighten all those connected with the manufacture of pulp and paper in order to keep it in the front ranks of industry.

MARTIN L. GRIFFIN

The Chemistry of the Non-benzenoid Hydrocarbons and Their Simple Derivatives. By BENJAMIN T. BROOKS. 612 pp. The Chemical Catalog Company, Inc., New York, 1922. Price, $7.00.

This volume is chiefly a compilation of detailed information regarding a wide range of hydrocarbons and derivatives not included in what is usually referred to as the benzene series. Much of the material presented is not found in the generally available textbooks of organic chemistry, and for this reason the book will undoubtedly be appreciated by chemists who lack the time or facilities to review original literature. It promises, also, to serve as a convenient bibliography of hydrocarbon chemistry.

The volume represents a tremendous amount of work, but it is obvious that the author has devoted more effort to the collection of his material than to the method of presenting it. The reviewer recognizes the impossibility of developing an absolutely satisfactory classification of all the types of compounds discussed, but believes, nevertheless, that it would be possible to effect considerable improvements in the arrangement employed in the present work.

The typographic make-up of the book could undoubtedly be improved, and a more judicious selection and systematic use of titles and sub-titles would be advantageous. Several instances of misspelling, probably due to insufficient care in proofreading, have been noted.

E. W. DEAN

Women in Chemistry. *A Study of Professional Opportunities.* 272 pp. Bureau of Vocational Information, 2 West 43rd St., New York, N. Y. Price, postpaid, paper bound, $1.10; cloth bound, $1.60.

This guide to the opportunities for woman in the various fields of chemistry will be of great help to those who are trying to decide upon a vocation. Too often the momentous choice is made by chance. It may be determined at the critical moment by a temporary liking for a particular study, by the influence of a teacher, by the example of a friend, by a casual newspaper item, or by the mere drift of circumstance. The sensible way of settling the question is to study the industry, its requirements and opportunities, its present pay and future prospects, and then to appraise frankly one's own capabilities and disposition for the situations attainable. But it is not human nature to proceed in such a rational manner in such important matters, and moreover the necessary data in regard to the conditions and openings in any given industry have not hitherto been made available. That excuse for ill-considered choice of vocation is now being removed by the Bureau of Vocational Information in such volumes as the present.

There are some 20,000 professional chemists in the United States and about a thousand of these are women. It is therefore a limited field but offers a new and congenial career to educated women. Those who have the genius for original research will find a free field in most institutions. For able and well-qualified women to teach chemistry there is a great demand, especially in connection with home economics. Women are doing well in analytical work in hospitals, industries, and government laboratories.

This volume discusses each of these fields and others, giving frankly its advantages and disadvantages, and telling what qualifications and training are needed and where the training can be obtained. Our readers will be interested in what Dr. Ruth Clark, a psychologist, finds to be the qualities most needed for success in the field of chemistry:

1—Mechanical ability and skill above the average.
2—A logical mind.
3—Enjoyment in solving concrete detail problems.
4—Physical health and endurance above the average.
5—Ability to work independently without supervision.
6—Ability to grasp large purposes.
7—Ability to work intellectually, without emotional interferences of a personal or social nature.
8—A critical point of view toward self and work.

EDWIN E. SLOSSON

Principles and Practice of Fur Dressing and Fur Dyeing. By WILLIAM E. AUSTIN. 191 pp. D. Van Nostrand Co., New York, 1922. Price, $4.00.

The dyeing and dressing of furs was formerly a European industry and previous to the war was of minor consideration in this country. However, owing to the serious dislocations of markets brought about by the war, the center of the fur industry has been transplanted to this country, with the result that the processing of furs here has now become an industry of large dimensions.

Fur dyeing and dressing has long been one of those "secret" arts practiced by handicraftsmen in a limited and closed guild. The literature heretofore available on this subject has been very meager.

The present volume gives us much better information than is obtainable from any preceding literature, and while the author has no doubt made good use of the sample cards issued by the various dyestuff manufacturers, he has also brought together a good deal of information that has doubtless been derived from his own experiences in the laboratory and factory. The methods of preparation used for getting the pelt into shape for dyeing are especially well considered. The actual processes of dyeing and dressing for the various types of furs are, however, rather sketchy and general in character. The book is well compiled and will be of value to the dyestuff chemist and others who desire to gain an elementary knowledge of fur dyeing. It should also be useful as a guide to students who are fitting themselves to become dyers of furs; in the latter case, however, it would be necessary to undergo considerable practical training in the handling and processing of furs.

To those dealing in and handling furs, who also desire to obtain some accurate information concerning their products, this volume will be of distinct value, as it will give them a better idea than they could otherwise obtain of the various processes and treatments necessary for the production of a finished fur.

J. MERRITT MATTHEWS

COMMERCE REPORTS

Notice: Commerce Reports are received by all large libraries and may be consulted there, or single numbers can be secured by application to the Bureau of Foreign and Domestic Commerce, Department of Commerce, Washington, D. C. The regular subscription rate for these Commerce Reports mailed weekly is $3.00 per year (10 cents per single copy), payable in advance to the Superintendent of Documents, Government Printing Office, Washington, D. C.

August

The following statistics are given showing the total imports of **petroleum products** into Germany: 1913, 81,743 tons; 1920, 253,358 tons; and for the 12 mo. ended April 1922, 812,956 tons. The 1913 exports appear to be considerably less than the post-war figures. (P. 381)

The consumption of **gasoline** in Latin-American countries is reviewed and statistics are given relative to consumption, production, and importation. (Pp. 381–3)

The consumption of **fertilizers** in Italy is described, and statistics given. (P. 383)

Prices of **phosphoric acid** in Germany are given. (P. 383)

Trieste is reported as a possible distribution center for Rumanian oil. (P. 384)

A translation of the new Peruvian regulations governing **petroleum** concessions is on file in the Petroleum Division of the Bureau of Foreign and Domestic Commerce. (P. 384)

A French presidential decree, dated June 14, modifies the **import duties** on the following products: fixed oils, pure; mineral wax or ozokerite; paraffin wax; aluminium sulfate; milk sugar; and manufactures of pure copper, brass, or other copper alloys not specified in the tariff. For the most part, the changes made are by way of reduction. (P. 408)

The Minister of Trade and Customs of Australia has issued a departmental by-law providing the conditions under which **amyl alcohol** and **fusel oil** may, when denatured, be exempted from excise duty. (P. 409)

The Sicilian **sulfur** industry is reviewed. (Pp. 414–5)

A merger has recently been effected between four important Italian companies manufacturing and trading in **tartaric acid.** (P. 416)

As a result of an exploring expedition, it has been definitely ascertained that **chicle** and **gutta percha** are to be found in the forests of the Amazon River District. (P. 421)

The organization of a Chemical Division in the Bureau of Foreign and Domestic Commerce is announced, the objects of the Division are stated, and export figures for the fiscal year are given for **chemicals** and **allied products, dyes** and **paints, medicines, fertilizers** and **naval stores.** (Pp. 432–3)

The German **potash** industry shows a considerable improvement since the beginning of the year, a demand for German potash having arisen in both the domestic and foreign market, particularly from America. (Pp. 433–4)

Mineral production in the province of Quebec during 1921 was curtailed by circumstances which affected all branches of the trade throughout the world. The following tabular statement shows the quantity and value of the production of mineral substances in that province during 1920 and 1921: (P. 453)

ARTICLES MINERAL SUBSTANCES	1920 Quantity	1920 Value	1921 Quantity	1921 Value
Asbestos, tons.........	179,891	$14,749,048	84,475	$5,199,789
[illegible], tons	19,716	43,559	12,397	14,536
Chromite, tons	10,580	247,730	1,893	22,696
Copper and sulfur ore, tons	14,186	98,854	1,986	10,463
[illegible], tons			1,167	8,001
[illegible] and fire-clay, tons	1,723	27,933	9,955	81,739
[illegible]	92	19,346	648	12,317
[illegible]	466,420	31,913	84,684	2,422
Magnesite, tons	17,941	512,755	4,984	74,110
Mica, lb	1,919,200	281,729	288,197	42,222
Mineral [illegible], tons	19,185	136,098	8,894	90,765
Mineral [illegible]	20,812	9,962	11,621	5,339
Phosphate, tons			30	453
Quartz and [illegible], tons	3,865	60,147	6,196	29,006
Silver, oz	14	58,052	39,327	21,339
Talc, tons	[illegible]	1,050	.....	.....
Titaniferous iron ore, tons	900	2,000		
Zinc and lead ore, tons	[illegible]	6,927	15,500	18,080

Improved transportation facilities are needed for the Algerian **phosphate mining** industry. (Pp. 453–4)

Statistics are given showing the **mineral** production of Italy for 1913, 1918, and 1921. (Pp. 454)

According to a cabled dispatch from the Commercial Attaché at Tokyo, no legislative action to protect the Japanese **dye** industry against foreign imports is likely for some time. (P. 482)

Proposed export duties on **iron** and **copper ores** included in a bill recently introduced in the Chilean Chamber of Deputies are given. (Pp. 483–4)

The provisions of the French law, by which by-products of **mineral oil** intended for feeding motors and for construction and maintenance of roads are admitted at a reduced rate of duty and under certain conditions, have been extended to Martinique. (P. 484)

A presidential decree extends indefinitely the concession for the importation of **gasoline** into Mexico free of duty. (P. 484)

Marked improvement is manifested in **chemicals** in France, with prices firmer and a strong demand. Many **wood distillation plants,** which were recently almost idle, are now working at full capacity, and the construction of new plants is planned. The **glue** industry is improving but exports of pharmaceutical products are meeting with severe German competition, particularly in South America. **Rosin** and **turpentine** prices are subject to considerable fluctuation, with a general upward tendency. (P. 511)

The production of **copper** in the Belgian Kongo in 1921 exceeded 30,000 metric tons, compared with 18,500 metric tons in 1920. This is said to be due to the high percentage of copper in the ore treated. (P. 518)

The **gasoline** trade of the Far East is reviewed and statistics are given showing the imports, exports, and consumption. (Pp. 528–9)

The Anglo-Persian Oil Company has obtained from the Greek government exclusive rights to drill for **oil** over the whole of Macedonia. (P. 530)

The Red Star Refineries at Montreal have secured the Canadian rights for the manufacture of a new product (Super-Gas), which it is claimed will supplant **gasoline.** (P. 530)

Talk is revived that the **oil shale** deposits of Pictou County, Nova Scotia, may be developed at an early date through the Anglo-Persian Oil Company. These shales are reported to be rich in oil, averaging from 20 to 100 gal. per ton, with valuable by-products in addition. (P. 530)

The Special Commissioner for Railways, Eastern Africa, has published an interesting statement showing comparative costs of **wood, coal,** and **oil** as locomotive fuel on the Uganda Railway. This report indicates that fuel oil would be more economical than wood and coal. (P. 530)

A number of German firms which formerly produced explosives for military purposes are now making **artificial silk** from various fabrics. (P. 532)

In general, there was an increase over last year in the quantity of **chemicals** imported into the United Kingdom during the first six months of 1922. The most important exceptions were crude glycerol, nickel oxide, sodium compounds, and cream of tartar. Statistics are given showing in detail the imports into and the exports from the United Kingdom for the six months ended June 1921 and June 1922. (Pp. 546–7)

There is said to be a good market for American **rosin** in Chile. (P. 547)

Caustic soda, liquid and solid, and **calcined soda** are no longer subject to the import license of Switzerland. (P. 559)

A rise in French naval stores prices is noted. Stocks of **turpentine** on hand seem to be limited, and the heavy rains in March and April greatly retarded distillation at the opening of the season. (P. 604)

During the past two or three months, large quantities of **caustic soda** have been received at the port of Hamburg, about one-half of which came from the United States. German importing concerns are purchasing all consignments obtainable, the reason apparently being the endeavor of soap, glass, and chemical factories to maintain their production at capacity. (P. 604)

The Chemical Division of the Bureau of Foreign and Domestic Commerce has received a copy of Report No. 7 of the Ministry of Munitions on the "Manufacture of Nitric Acid from Niter and Sulfuric Acid." This report is based on experiments and records of the British government plants during the war and is said to be of interest to domestic manufacturers of nitric acid. A copy of this report may be borrowed from the Chemical Division for a short time. (P. 604)

Prices for **sulfuric acid** in Germany have been fixed by the committee for the control of sulfuric acid at 245 marks for producers and 270 marks for consumers for each 100 kilos of 60° sulfuric acid. (P. 604)

The **petroleum** trade of the Fiume District is reviewed. (P. 605)

The outstanding features of the **petroleum** import trade of the United Kingdom continue to be the increases in the imports of crude petroleum and of motor spirit. (P. 605)

The **petroleum** price war has now been settled in Japan by an agreement among the companies. (P. 606)

There has been a progressive increase in the production of **mineral oil** in France since the first part of 1921. The production for the first three months of 1922 is said to have been 53 per cent above that for the corresponding period of 1921. (P. 606)

The tax on **copra** exported from Fiji has been reduced. (P. 620)

The government of British Honduras has established a King's warehouse temporarily for **inflammable liquids.** (Pp. 621–2)

A good market is reported in Japan for **soaps, perfumes,** and **toilet articles.** (P. 627)

SPECIAL SUPPLEMENTS ISSUED

CZECHOSLOVAKIA
GUATEMALA
FRANCE
HONGKONG
RUSSIAN FOREIGN TRADE

"Rubber Situation in British Colonies and Protectorates." *Trade Information Bulletin* **49.**

"Rumanian Petroleum Industry in 1921." *Trade Information Bulletin* **45.**

STATISTICS OF EXPORTS TO THE UNITED STATES

LONDON—(P. 497)		CANADA—(P. 537)
Tin	Rubber	Wood pulp
Drugs and chemicals	Leather	Pulp wood
	Hides	

CURRENT PUBLICATIONS

NEW BOOKS

Analytical Chemistry: Trattato di Chimica Analitica Applicata. Vol. II. G. V. VILLAVECHIA. 2nd edition, revised and enlarged. 884 pp. Price, paper, 58 lire. U. Hoepli, Milan.

Chemical Analysis: Standard Methods of Chemical Analysis. Vols. I and II. WILFRED W. SCOTT. 714 and 680 pp. Price, $10.00. D. Van Nostrand Co., New York.

Chemistry: The Science of Matter and Its Changes. HIPPOLYTE GRUENER. 384 pp. Illustrated. Price $3.00. Harper & Bros., New York.

Chemistry: Second Year College Chemistry. A Manual of Laboratory Exercises. WILLIAM H. CHAPIN. 122 pp. Illustrated. Price, $1.50. John Wiley & Sons, Inc., New York.

Dust Explosions. DAVID J. PRICE AND HAROLD H. BROWN. 320 pp. Illustrated. Price, $3.00. National Fire Protection Association, Boston.

Electrochemistry: Grundzüge der Angewandten Elektrochemie. Vol. I—Elektrochemie der Lösungen. G. GRUBE. 268 pp. Price, paper, 8s. 6d.; bound, 10s. 3d. Th. Steinkopff, Dresden and Leipzig.

Evolution of Atoms and Isotopes. W. D. Verschoyle. 49 pp. Price, 1s. 9d. J. J. Keliher and Co., Ltd., London.

Explosives: Technical Records of Explosives Supply. 1915 to 1918. No. 7. Manufacture of Nitric Acid from Nitric and Sulfuric Acid. 86 pp. H. M. Stationery Office, London. Price, 11s.

Filtration. T. ROLAND WOLLASTON. 102 pp. Price, 2s. 6d. Sir Isaac Pitman & Sons, Ltd., London.

Glass: Experimental Researches and Reports. Vol. IV, 1921. DEPT. OF GLASS TECHNOLOGY, The University, Sheffield. 118 pp.

Inorganic Chemistry. H. G. DENHAM. 683 pp. Price, 12s. 6d. Edward Arnold & Co., London.

Liquid Fuel and Its Apparatus. WILLIAM H. BOOTH. 2nd edition. 308 pp. Price, $4.00. E. P. Dutton & Co., New York.

Mechanical Handling and Storing of Material. G. F. ZIMMER. 804 pp. Crosby, Lockwood & Son, London.

Paint: Proceedings of the Scientific Section, Educational Bureau. HENRY A. GARDNER, Director. 481 pp. Price, $6.00. Quantity limited. Institute of Paint and Varnish Research, Washington, D. C.

Paint: Pour le Peintre-Vitrier: Origine, Composition et Propriétés des Matières Premières Recettes, Formulas, Procédés, "Trucs" et Tours de Main du Praticien. ED. BATAILLE, A. CHAPLET, AND J. DE THELLESME. 164 pp. Illustrated. Price, 7 fr. Dunod, Paris.

Paint: Couleurs, Peintures et Vernis. J. DESALME AND L. PIERRON. 455 pp. Illustrated. Price, 15 fr. Dunod, Paris.

Patent Business: A Comprehensive Instruction Course in Ten Lessons; Written for Those Who Have the Gift of Inventive Talent, and the Ambition to Supplement That Gift with a Working Knowledge of the Business of Obtaining Sound and Salable Patents as a Lifetime Occupation. Vol. I. CHARLES O. TESSIER. 155 pp. Price, $3.00. C. O. Tessier, Cleveland, Ohio.

Potter's Craft. CHARLES F. BINNS. 206 pp. Price, $2.50. D. Van Nostrand Co., New York.

Proceedings of the Physical Society of London. Vol. 34, Part 5. 30 pp. Price, 6s. The Fleetway Press, London.

Quicksilver, 1913–1919. The Mineral Industry of the British Empire and Foreign Countries. War Period. IMPERIAL MINERAL RESOURCES BUREAU. Price, 1s. H. M. Stationery Office, London.

Rolling Mill: Études sur les Laminoirs. J. PUPPE. 307 pp. Price, 70 fr. Dunod, Paris.

Wood Preserving Terms. ERNEST F. HARTMAN AND E. F. PADDOCK. 85 pp. Price, paper, $1.00. Protexol Corporation, New York.

RECENT JOURNAL ARTICLES

Accuracy of Boiler Tests. ALFRED COTTON. *The Coal Industry,* Vol. 5 (1922), No. 8, pp. 367–71.

Art of Alloying. W. GUERTLER. *Brass World,* Vol. **17** (1922), No. 8, pp. 229–34. Abstracted from *Zeitschrift für Metallkunde,* Vol. 9 (1921), p. 257.

Atomic Structure: The Stability of Atom Nuclei, the Separation of Isotopes, and the Whole Number Rule. WILLIAM D. HARKINS. *Journal of the Franklin Institute,* Vol. **194** (1922), No. 2, pp. 165–211.

Ammoniacal Liquor Stills: Observations on the Design and Working of Ammoniacal Liquor Stills. P. PARRISH. *Journal of the Society of Chemical Industry,* Vol. **41** (1922), No. 14, pp. 229T–42T.

Catalysts: Notes on the Poisoning of Catalysts. ALWYN PICKLES. *The Chemical Age (London),* Vol. **7** (1922), No. 164, pp. 164–65.

Chalcedony: The Products of the Calcination of Flint and Chalcedony. EDWARD W. WASHBURN AND LOUIS NAVIAS. *Journal of the American Ceramic Society,* Vol. **5** (1922), No. 9, pp. 565–85.

Chemical Change and Catalysis. Rhapsodies Culled from the Thionic Epos. HENRY E. ARMSTRONG. First Messel Memorial Lecture. *Journal of the Society of Chemical Industry,* Vol. **41** (1922), No. 15, pp. 253T–70T.

Chemistry and the Destruction of Pests in Agriculture. L. CARPENTER. *The Chemical Age (London),* Vol. **7** (1922), No. 166, pp. 233–34.

Coal: The Constitution of Coal. MARIE CARMICHAEL STOPES. *The Canadian Mining Journal,* Vol. **43** (1922), No. 31, pp. 505–06.

Dye Situation in Great Britain, and Elsewhere. ELLWOOD HENDRICK. *Chemical and Metallurgical Engineering,* Vol. **27** (1922), No. 10, pp. 494–96.

Evaporation: The General Problem of Evaporation. J. W. HINCHLEY. *Journal of the Society of Chemical Industry,* Vol. **41** (1922), No. 14, pp. 242T–46T.

Ferrotungsten: Analise Rapida del Ferro-tungsteno. LUIGI LOSANA AND ENRICO CAROZZI. *Giornale di Chimica Industriale ed Applicata,* Vol. **4** (1922), No. 7, pp. 299–301.

Fuel Oil: Distribution of Fuel Oil in Industrial Plants. J. A. BROWN. *Forging and Heat Treating,* Vol. **8** (1922), No. 8, pp. 336–40.

Glass: The British Glass Industry: Its Development and Its Outlook. W. E. S. TURNER. *Journal of the Society of Glass Technology,* Vol. **6** (1922), No. 22, pp. 108–46.

Glass: A Critical Review of the Provisional Specifications for Glass Refractory Materials. W. J. Rees. *Journal of the Society of Glass Technology*, Vol. 6 (1922), No. 22, pp. 181–204.

Glass: The Effect of Absorbed Gas on the Conductivity of Glass. V. [illegible] *Journal of the Franklin Institute*, Vol. 194 (1922), [illegible]

Glass: The Production of Colourless Glass in Tank Furnaces with Particular Reference to the Use of Selenium. Part I. A. Cousen and W. [illegible] *Journal of the Society of Glass Technology*, Vol. 6 (1922), No. 22, [illegible]

Leather: Science of Hide Curing. George D. McLaughlin and Edwin R. Theis. *Journal of the American Leather Chemists' Association*, Vol. 17 (1922), No. 8, pp. 376–99.

Leaching Ore with Sulfur Dioxide. Joseph Irving, Jr. *Engineering and Mining Journal-Press*, Vol. 114 (1922), No. 9, pp. 360–61.

Lime for Glass-Making. R. R. Shively. *The Glass Industry*, Vol. 3 (1922), No. 8, pp. 154–56.

Lubricants: Technical Examination of Lubricating Oil and Grease. F. W. Watson and H. D. Bell. *The Journal of the Chemical, Metallurgical and Mining Society of South Africa*, Vol. 22 (1922), No. 11, pp. 211–19.

Paper: Rosin Size Control. P. W. Codwise. *Paper*, Vol. 30 (1922), No. 23, pp. 7–9.

Rubber: Accelerated Aging Tests on Rubber Goods. W. W. Evans. *The Rubber Age*, Vol. 11 (1922), No. 10, pp. 345–47.

Rubber: Scientific Management for Rubber Manufacturers. Standardization. Alfred Baruch. *The Rubber Age*, Vol. 11 (1922), No. 10, pp. 348–51.

Steel: The Annealing of Tool Steels. Arthur W. F. Green. *Forging and Heat Treating*, Vol. 8 (1922), No. 8, pp. 346–53.

Steel: The Making, Forging, and Heat Treating of Nickel Chromium Steels. Harry Brearley. *Forging and Heat Treating*, Vol. 8 (1922), No. 8, pp. 341–45.

Textiles: The Acid Treatment of Cotton Fabrics for the Production of Special Finish. Barrington De Puyster. *Color Trade Journal*, Vol. 11 (1922), No. 2, pp. 54–59.

Titration: Studies in the Titration of Acids and Bases. J. L. Lizius. *The Analyst*, Vol. 47 (1922), No. 557, pp. 331–41.

Wood: The Effect of Chemicals on the Ignition Temperature of Wood. W. O. Banfield and W. S. Peck. *Canadian Chemistry and Metallurgy*, Vol. 6 (1922), No. 8, pp. 172–76

GOVERNMENT PUBLICATIONS

Notice—*Publications for which price is indicated can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C. Other publications can usually be supplied from the Bureau or Department from which they originate.*

Bureau of Mines

Comminuted Smokeless Powder as a Blasting Agent. C. E. Munroe and [illegible] *Reports of Investigations* 2386. 19 pp. Issued August 1922.

Compressed-Air Illness and Its Engineering Importance with a Report of Cases at the East River Tunnels. Edward Levy. *Technical Paper* 285. [illegible]

Experimental Production of Alloy Steels. H. W. Gillett and E. L. Mack. [illegible] 199. [illegible]

Explosives Used in June 1922. W. W. Adams. *Reports of Investigations* 2387. [illegible] pp. Issued August 1922.

Fatalities at Coal Mines in June 1922. W. W. Adams. *Reports of Investigations* 2379. [illegible] pp. Issued July 1922.

Fuel Economy from Old Plant Equipment. A. R. Mumford. *Reports of Investigations* 2373. [illegible] pp. Issued July 1922.

Inclusions in Aluminium-Alloy Sand Castings. R. J. Anderson. *Technical Paper* 290. [illegible] Paper, 10 cents.

Keeping Up-to-Date in Safety Methods in Coal Mining. D. Harrington. *Reports of Investigations* 2372. 2 pp. Issued July 1922.

Permissible Explosives, Mining Equipment, and Apparatus, Approved Prior to March 15, 1922. S. P. Howell, L. C. Ilsley, D. J. Parker, and A. C. [illegible] 307. [illegible] pp. 1922. Paper, 5 cents.

Production of Explosives in United States, Calendar Year 1921, with Notes on Mine Accidents Due to Explosives. W. W. Adams. *Technical Paper* [illegible]

Recent Progress in the Thawing of Frozen Gravel in Placer Mining. Chas. [illegible] Paper, 10 cents.

Safe Mechanical Equipment for Use in Shaft Sinking. R. H. Kudlich. [illegible] 5 cents.

Sixth Semiannual Motor Gasoline Survey. A. D. Bauer and N. F. Le Jeune. [illegible] 2388. 9 pp. Issued August 1922.

Storage and Transportation of Portland Cement. (With a Bibliography.) W. M. Myers. *Reports of Investigations* 2377. 5 pp. Issued July 1922.

Summary of Investigations of Dust and Ventilation in Metal Mines. (With a Bibliography.) *Reports of Investigations* 2374. 6 pp. Issued July 1922.

The Rate of Reduction of Hematite to Magnetite by Methane. C. M. Bouton. *Reports of Investigations* 2381. 9 pp. Issued August 1922.

Why Miners' Portable Electric Lamps Require Safety Devices. L. C. Ilsley. *Reports of Investigations* 2371. 9 pp. Issued July 1922.

Bureau of Standards

Practical Spectrographic Analysis. W. F. Meggers, C. C. Kiess, and F. J. Stimson. *Scientific Paper* 444. 1922. Paper, 10 cents.

Radiators for Aircraft Engines. S. R. Parsons and D. R. Harper, 3rd. *Technologic Paper* 211. 183 pp. Paper, 50 cents.

The Spectral Transmissive Properties of Dyes: I—Seven Permitted Food Dyes, in the Visible, Ultraviolet, and Near Infra-Red. K. S. Gibson, H. J. McNicholas, E. P. T. Tyndall, M. K. Frehafer, with the cooperation of W. E. Mathewson. *Scientific Paper* 440. 184 pp. Paper, 15 cents.

United States Government Specification for Automobile Soap. *Circular* 127. Paper, 5 cents.

United States Government Specification for Basic Carbonate White Lead, Dry and Paste, Federal Specifications Board, Standard Specification 5. Officially adopted by Federal Specifications Board, February 3, 1922, for use of departments and independent establishments of the Government, in purchase of materials covered by it. *Circular* 84. 2nd ed. 8 pp. Paper, 5 cents.

United States Government Specification for Chip Soap. *Circular* 128. 1922. Paper, 5 cents.

United States Government Specification for Flat Interior Lithopone Paint, White and Light Tints, Federal Specifications Board, Standard Specification 21. Officially Adopted by Federal Specifications Board, February 3, 1922, for use of departments and independent establishments of the Government in purchase of materials covered by it. *Circular* 111. 3rd ed. 8 pp. Paper, 5 cents.

United States Government Specification for Grit Cake Soap. *Circular* 130. 1922. Paper, 5 cents.

United States Government Specification for Hand Grit Soap. *Circular* 130. 1922. Paper, 5 cents.

United States Government Specification for Interior Varnish, Federal Specifications Board, Standard Specification 22. Officially adopted by Federal Specifications Board, February 3, 1922, for use of departments and independent establishments of the Government in purchase of materials covered by it. *Circular* 117. 6 pp. Paper, 5 cents.

United States Government Specification for Iron-Oxide and Iron-Hydroxide Paints, Federal Specifications Board, Standard Specification 13. Officially adopted by Federal Specifications Board, February 3, 1922, for use of departments and independent establishments of the Government in purchase of materials covered by it. Circular 93. 2nd ed. 9 pp. 1922. Paper, 5 cents.

United States Government Specification for Leaded Zinc Oxide, Dry and Paste, Federal Specifications Board, Standard Specification 9. Officially adopted by Federal Specifications Board, February 3, 1922, for use of departments and independent establishments of the Government in purchase of materials covered by it. *Circular* 88. 2nd ed. 8 pp. 1922. Paper, 5 cents.

United States Government Specification for Linseed Oil, Raw, Refined, and Boiled, Federal Specifications Board, Standard Specification 4. Officially adopted by Federal Specifications Board, February 3, 1922, for use of departments and independent establishments of Government in purchase of materials covered by it. *Circular* 82. 2nd. ed. 9 pp. Paper, 5 cents.

United States Government Specification for Liquid Soap. *Circular* 124. 1922. Paper, 5 cents.

United States Government Specification for Ocher, Dry and Paste, Federal Specifications Board, Standard Specification 12. Officially adopted by Federal Specifications Board, February 3, 1922, for use of departments and independent establishments of the Government in purchase of materials covered by it. *Circular* 91. 2nd ed. 8 pp. Paper, 5 cents.

United States Government Specification for Ordinary Laundry Soap. *Circular* 129. 1922. Paper, 5 cents.

United States Government Specification for Salt Water Soap. *Circular* 126. 1922. Paper, 5 cents.

United States Government Specification for Scouring Compounds, for Floors (*a*) and (*b*), and Soap Scouring Compound (*c*). *Circular* 131. 1922. Paper, 5 cents.

United States Government Specification for Soap Powder. *Circular* 125. Paper, 5 cents.

United States Government Specification for White Floating Soap. *Circular* 123. Paper, 5 cents.

Bureau of the Census

Glucose and Starch. 14th Census of the United States: Manufacturers, 1919. Prepared under the supervision of E. F. Hartley. 8 pp. 1922.

Gold, Silver, Copper, Lead, and Zinc. 14th Census of the United States: Mines and Quarries, 1919. Prepared under the supervision of E. F. Hartley by F. J. Katz. 33 pp. 1922.

Iron Ore. 14th Census of the United States: Mines and Quarries, 1919. Prepared under the supervision of E. F. Hartley by F. J. Katz. 25 pp. 1922.

Petroleum and Natural Gas. 14th Census of the United States: Mines and Quarries, 1919. Prepared under the supervision of E. F. Hartley by F. J. Katz. 31 pp. 1922.

Petroleum Refining. 14th Census of the United States: Manufactures, 1919. Prepared under the supervision of E. F. Hartley. 11 pp., 1922.

Congress

An Act, to regulate revenue, to regulate commerce with foreign countries, to encourage the industries of the United States, and for other purposes. *H. Rpt.* **7456.** August 19, 1922. Ordered to be printed with the amendments of the Senate numbered. 476 pp.

A Bill, to improve the navigability of waters of the United States by preventing oil pollution thereof. *S.* **3968.** Introduced by Mr. Frelinghuysen on August 30, 1922. Read twice and referred to the Committee on Commerce. 4 pp.

Muscle Shoals. Mr. Ladd (for himself and Messrs. Capper, Harrison, Caraway, Ransdell, Heflin, and Smith), from the Committee on Agriculture and Forestry, submitted views to accompany S. J. Res. 227. Calendar 817. *S. Rpt.* **831.** Part 2. 19 pp. August 4, 1922.

Muscle Shoals. Hearings on S. 3420, for manufacture of explosives, for use of Army and Navy, for manufacture of fertilizer, for agricultural purposes, to incorporate Federal Chemical Corporation, and for other purposes; and on the Henry Ford Muscle Shoals offer, offer made by the Alabama Power Co., proposing to complete Wilson Dam, the offer of Frederick E. Engstrum for Muscle Shoals, and offer of Charles L. Parsons for properties at Muscle Shoals, Ala. 949 pp. 1922.

Muscle Shoals. Report to accompany S. J. Res. 227 (rejecting bids for acquisition of Muscle Shoals); submitted by Mr. Norris, April 20, 1922, calendar day July 20, 1922. *S. Rpt.* **831.** Part 1. 36 pp.

Saltpeter, Chile. Nitrate of soda imports from Chile to United States, extracts from hearings, 66th Congress, 2nd Session, and 67th Congress, 2nd session. 1 p.

Water Pollution. Preventing the Oil Pollution of Navigable Waters of the United States. *S. Rpt.* **901,** to accompany S. 3968. August 31, 1922. 3 pp.

Department of Agriculture

By-products from Crushing Peanuts. J. B. Reed. *Department Bulletin* **1096.** 12 pp. Issued August 12, 1922.

Digestibility of Cod-Liver, Java-Almond, Teaseed, and Watermelon-Seed Oils, Deer Fat, and Some Blended Hydrogenated Fats. H. J. Deuel, Jr. *Department Bulletin* **1033.** 15 pp. Paper, 15 cents. Issued July 27, 1922.

Rules and Regulations for the Enforcement of the Federal Food and Drugs Act. *Circular* 21. Office of the Secretary. 8th revision. 27 pp. Issued August 7, 1922.

Some Experiments with a Boric Acid-Canning Powder. R. B. Edmondson, Charles Thom, and L. P. Giltner. *Department Circular* 237. 12 pp. Issued August 31, 1922. Paper, 5 cents.

Federal Trade Commission

Petroleum Trade in Wyoming and Montana. Letter transmitting, pursuant to law, report on conditions in petroleum trade in Wyoming and Montana (with draft of bill to prevent evasions of antitrust laws). *S. Doc.* **233.** 4 pp. 1922.

Geological Survey

Bauxite and Aluminium in 1921. J. M. Hill. Separate from Mineral Resources of the United States, 1921, Part 1. 8 pp. Published August 1, 1922.

Clay-Working Industries, Clay, and Silica Brick in 1919 and 1920. Jefferson Middleton. Separate from Mineral Resources of the United States, 1920, Part 2. 37 pp. Published August 14, 1922.

Gypsum in 1921. K. W. Cottrell. Separate from Mineral Resources of the United States, 1921, Part 2. 8 pp. Published August 4, 1922.

Magnesite in 1921. C. G. Yale. Separate from Mineral Resources of the United States. 1921, Part 2. 6 pp. Published August 5, 1922.

Mica in 1921. B. H. Stoddard. Separate from Mineral Resources of the United States, 1921, Part 2. 6 pp. Published August 3, 1922

Oil and Gas Prospects in and near the Crow Indian Reservation, Montana. W. T. Thom, Jr. *Bulletin* **736-B.** Separate from Contributions to Economic Geology, 1922, Part 2. 19 pp. Published July 6, 1922.

Quicksilver in 1921. F. L. Ransome. With a Bibliography by I. P. Evans. Separate from Mineral Resources of the United States, 1921, Part 1. 14 pp. Published August 7, 1922.

Tin in 1921. B. L. Johnson. Separate from Mineral Resources of the United States, 1921, Part 1. 3 pp. Published August 1, 1922.

Interior Department

Naval Reserve Oil Leases, in Response to Resolution. Communication submitting information concerning Naval Reserve Oil Leases. *S. Doc.* **210.** 42 pp. 1922.

Public Health Reports

Ohio Law for Enforcing Correction of Stream Pollution and Improvement of Public Water Supplies. *Public Health Reports,* **37** (August 11, 1922), 1945–50.

Physiological Effects of Exposure to Low Concentrations of Carbon Monoxide. R. R. Sayers, F. V. Meriwether, and W. P. Yant. *Reprint* **748.** 16 pp. Paper, 5 cents.

Preparation and Administration of Arsphenamine and Neoarsphenamine. Standard Instructions for the Preparation and Intravenous Administration of Arsphenamine and Neoarsphenamine for Use by the Medical Departments of the Army, of the Navy, and of the Veterans' Bureau, and by the Public Health Service. *Public Health Reports,* **37** (August 4, 1922), 1867–82.

Report on the Public Water Supply of Delaware, Ohio. Report of an Investigation Made by the Engineering Division of the Ohio State Department of Health. F. H. Waring. *Public Health Reports,* **37** (August 11, 1922), 1933–45.

Stream Pollution Investigations. Recommendations as to Plan and Policy made by United States Public Health Service Consultants in Stream Pollution Investigation Work. *Public Health Reports,* **37** (August 25, 1922), 2049–53.

Tariff Commission

Tariff Information Surveys. Revised edition, 1922. On articles in Paragraph 359 of the Tariff Act of 1913 and related articles in other paragraphs.

N-15. Heavy Leathers. 48 pp. Paper, 5 cents.
N-16. Light Leathers, Group 1. 54 pp. Paper, 5 cents.

The Foreign Commerce Department of the Chamber of Commerce of the United States has just issued a foreign commerce handbook, which contains a great deal of valuable information as to sources of service in foreign trade. The book also contains a list of the topics of national importance that are engaging the attention of the Chamber's Foreign Commerce Department Committee.

Zinsser & Co., Hastings-on-Hudson, N. Y., are now manufacturing Aczol, a wood preservative which has been in use in Belgium and continental Europe for several years. The name is derived from its ingredients—ammonia, copper, zinc, and phenol. Records of the use of wood impregnated with Aczol have been kept in Belgium for the past decade, and it is claimed to be very efficient, particularly in coal mine timbers, wood paving blocks, and railroad ties.

A company is being organized to manufacture potassium phosphate under the Kreiss patents at Jacksonville, Fla. Work on a $75,000 plant will begin shortly. The company will not manufacture complete fertilizers, but will sell the potassium phosphate to fertilizer manufacturers. The officers are: president, E. R. Taber; vice president, William B. Taber; secretary and treasurer, Charles N. Welshans.

E. I. du Pont de Nemours & Co. have announced the development of a dye known as Pontamine Brown CR, a direct dyestuff which produces reddish brown shades on cotton and may also be used on artificial silk.

Chemical fumes coming in contact with the flame of a night watchman's oil lamp are believed to have caused a fire which wrecked one of the buildings of the Verona Chemical Company plant at Newark, N. J., on September 1. The damage is estimated at $100,000.

MARKET REPORT—SEPTEMBER, 1922

[Supplied by Drug & Chemical Markets]

September has seen a steady strengthening in the tone of chemical markets, with a more decided upward trend to prices. Practically all the important movements during the month have been toward higher levels. Both heavy chemicals and medicinals have shared in the improved position, while intermediates and dyestuffs have continued to remain dormant. The tariff situation has naturally held the center of the stage, and, although there was some movement of goods based on rates which were considered certain prior to passage, the general attitude of consumers was to wait for definite certainties. In the chemical markets generally over a period of a month past, 80 per cent or more of all price movements have been to higher levels.

Many prices were advanced in anticipation of the tariff,—that is, the higher cost of raw materials which in a number of cases was caused by speculative buying before the higher rates went into effect, drove up figures for finished goods. A number of prices were advanced, owing to scarcities of spot goods developing through the long inactivity in manufacturing circles, permitting stocks to become almost depleted. Most consumers preferred to pay the higher prices for spot goods rather than gamble on contract supplies, with the tariff uncertainty hovering over them. Increased activity in chemical-consuming manufacturing circles broadened the hand-to-mouth buying for immediate needs and played its part in the reduction of available stocks.

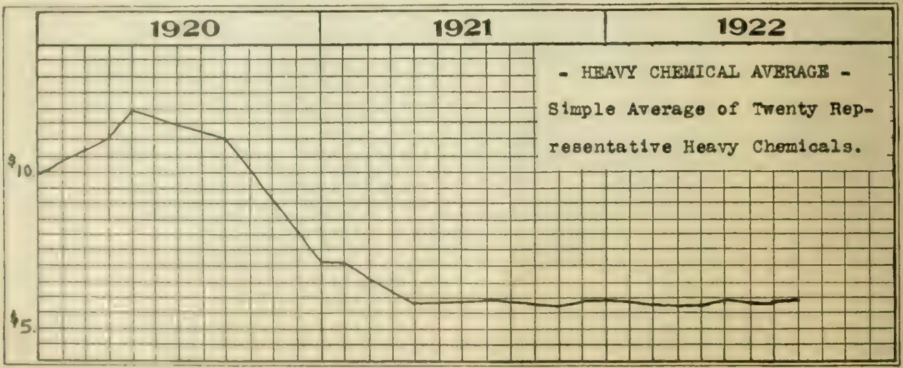
Among the heavy chemicals, the mineral acids have remained unchanged and quiet. Caustic soda held strong throughout the month, but softened slightly at the close, owing to cheaper offerings in outside hands. Soda ash has been steady with a consistently good demand. Copper sulfate supplies are still closely held and not overabundant. Bleaching powder has been extremely scarce, especially on the spot, and has moved upward in price on this account from $1.75 to $2.00 per hundred. Arsenic prices have held tight with an advancing tendency, although the consuming season is about over. Through the season, supplies have been inadequate to supply the growing demand for this product. This year the particularly heavy demand for calcium arsenate in the cotton fields took all available arsenic supplies.

Both sodium and potassium prussiates have reached higher prices during the month. Yellow potassium prussiate moved up to 36 cents a pound spot. Bichromates are slightly higher than they were during August. Salt cake has continued scarce. Supplies of copperas, some months ago a drug on the market here, have been cleaned up and are now very small. Producers of oxalic acid have moved their prices up to 17 cents a pound, f. o. b. works, during the month. Of the alums, ammonia is higher while the others have remained unchanged. Both ammonium sulfate and gray sal ammoniac have gained in price, as spot supplies have been taken up without replacement. In fact, all ammonium products have been strong as a result of lack of activity in the by-product plants. Little has happened in caustic potash and the market has remained quiet. Taken all in all, industrial chemical prices have gained 1 or 2 per cent during September.

Of the oils, linseed has held strong in spite of the fact that most of the big buyers have been holding off for lower prices. The price stands slightly higher than it did at the beginning of the month. Menhaden strengthened slightly on some buying. Cottonseed oil continues quiet. Turpentine moved up during the month from $1.23 a gallon to $1.32 after numerous fluctuations. A few minor fluctuations in rosin during the month found the price little changed at the close.

Phenol, because of its scarcity and high price for some two months past, is worthy of special attention at this time. Spot supplies of crystals are practically impossible to find on the open market. A few odd lots are available, but the only quantity stocks are reported held by two leading consumers who are evidently not anxious to sell. Licenses for import from Europe have been issued, but owing to the uncertainty of getting supplies, the new tariff rate, and the higher prices ruling abroad, consumers here are hesitating to bring in stocks. A well-known manufacturer is reported to have resumed manufacturing synthetic phenol, but if the report is true, none has yet been offered on the market from this source. Prices for odd lots of spot crystals in large drums stand to-day at 20 cents at 22 cents a pound.

In the fine chemicals, advances have been scored by the salicylates, as might be expected with the present market for phenol. The sharp rise in quicksilver prices on the almost certain prospects of an $18.75 a flask duty, forced manufacturers of mercurials to move up their prices. Glycerin has climbed steadily. Resorcinol is higher. Wood alcohol is up sharply. Surplus stocks of formaldehyde have been cleaned out and prices are higher with goods hard to find. After a long period of weakness, hydroquinone moved up sharply. Iodine and the iodides were advanced during the month; the syndicate figure for crude iodine has been revised upward. Acetone has gone up. Imported citric and tartaric acids and cream of tartar rose on higher import cost. Bismuth salts were advanced twice in the month.



Courtesy of Drug & Chemical Markets

FIRST-HAND PRICES FOR GOODS IN ORIGINAL PACKAGES PREVAILING IN THE NEW YORK MARKET

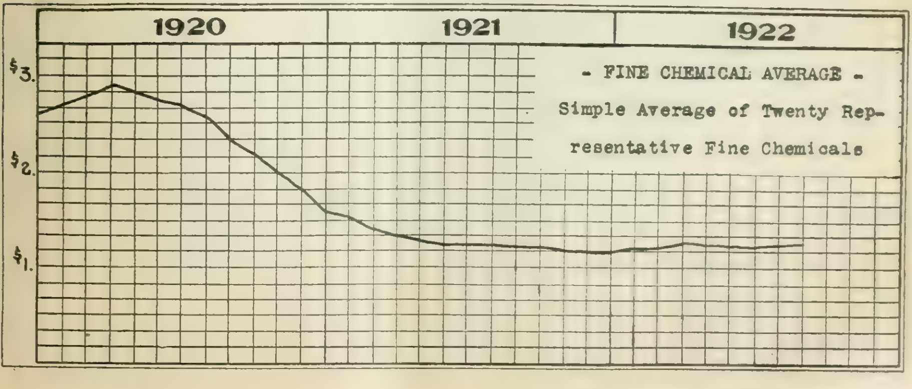
INORGANIC CHEMICALS

	Sept. 1	Sept. 15	Jan. 1922
Acid, Boric, cryst. bbls.......lb.	.11¾	.11¾	.12¾
Hydrochloric, comm'l. 20° lb.	.01¼	.01¼	.01¼
Hydrofluoric, 30% bbls..lb.	.07	.07	.07
Hydriodic, sp. gr. 1.150...lb.	2.25	2.25	2.00
Nitric, 42°, cbys. c/l wks.lb.	.06	.06	.06
Phosphoric, 50% tech.....lb.	.07½	.08	.10
Sulfuric, C. P............lb.	.08	.07	.07
66° tks. wks........ton	16.00	16.00	16.00
Oleum 20%.........ton	19.00	19.00	19.00
Alum, Ammonia, lump........lb.	.03¼	.03½	.03½
Potash, lump............lb.	*.03	*.03	*.03½
Chrome............lb.	.06	.06½	.07
Soda, ground............lb.	.03½	.03½	.03½
Aluminium Sulfate (iron-free).lb.	.02½	.02½	.02½
Ammonium Carbonate, pwd...lb.	.08½	.07	.08
Chloride, white gran......lb.	.07¾	.07¾	.07½
Ammonia, anhydrous........lb.	.30	.30	.30
Ammonia Water, drums, 26°...lb.	.07½	.07½	.07½
Arsenic, white...............lb.	.08½	.08½	.06½
Barium Chloride............ton	*85.00	*85.00	*53.00
Nitrate.................lb.	*.08	*.08	*.07
Barytes, white..............ton	33.50	33.50	28.00
Bleaching Powd., 35%, works ....100 lbs.	1.75	2.00	2.25
Borax, cryst., bbls............lb.	.05½	.05½	.05¾
Bromine, pure, wks...........lb.	.28	.28	.23
Calcium Chloride, fused, f.o.b. N. Y....................ton	24.50	24.50	28.75
Chlorine, liquid..............lb.	.06	.06	.06
Copper Sulfate..........100 lbs.	7.00	7.00	5.55
Iodine, resublimed...........lb.	4.20	4.40	3.80
Lead Acetate, white crystals...lb.	.10½	.10½	.11
Nitrate.................lb.	.22	.22	.15
Red.....................lb.	.08	.08	.08
White (Carb.)............lb.	.07¼	.07¼	.07¼
Lime Acetate............100 lbs.	2.35	2.35	1.75
Magnesium Carbonate, tech...lb.	.06	.06	.06
Magnesite, calcined..........ton	55.00	55.00	55.00
Phosphorus, yellow...........lb.	*.25	*.25	*.27
Red.....................lb.	*.26	*.26	*.30
Plaster of Paris.............bbl.	4.25	4.25	4.25
Potassium Bichromate........lb.	.09¾	.09¾	.10½
Bromide, imported.......lb.	*.13	*.14	*.13
Carbonate, calc., 80–85% .lb.	*.04¾	*.04¾	*.04½
Chlorate, cryst...........lb.	*.06½	*.07	*.05½
Hydroxide, 88–92%......lb.	*.05¾	*.05¾	*.06
Iodide, bulk.............lb.	3.30	3.50	2.90
Nitrate.................lb.	.08	.08	.08
Permanganate, U. S. P....lb.	*.14½	*.15	*.15
Prussiate, red............lb.	*.90	*.90	*.29
Yellow.............lb.	*.33	*.35	*.24½
Salt Cake, bulk.............ton	18.00	18.00	17.00
Silver Nitrate...............oz.	.47½	.46½	.44½
Soda Ash, 58%, bags.....100 lbs.	*1.80	*1.80	*1.85
Caustic, 76%, N. Y..100 lbs.	3.60	3.60	3.80
Sodium Acetate..............lb.	.06	.06	.04
Bicarbonate.........100 lbs.	2.00	2.00	2.00
Bichromate..............lb.	.07	.07½	.07¾
Bisulfite, powd...........lb.	.04¼	.04¼	.04¼
Chlorate................lb.	.06¾	.07	.07½
Cyanide, 96–98%........lb.	.23	.23	.28
Fluoride, tech ....lb.	.09½	.09½	.09½
Hyposulfite, bbls.....100 lbs.	2.00	2.00	3.50
Nitrate, 95%........100 lbs.	2.55	2.55	2.32½
Nitrite..................lb.	.09½	.09½	.06½
Prussiate, yellow.........lb.	.22	.23½	.16½
Phosphate (di-sod.),tech..lb.	.04	.04½	.04¼
Silicate, 40°.............lb.	.01½	.01½	.01½
Sulfide, 60%, fused.......lb.	.04	.04	.05
Strontium Nitrate............lb.	*.10	*.10	*.10
Sulfur, flowers...........100 lbs.	3.00	3.00	2.75
Crude, mines.......long ton	14.00	14.00	16.00
Tin Bichloride, 50% sol'n......lb.	.10½	.10½	.09¼
Oxide...................lb.	.38	.38	.37
Zinc Chloride, U. S. P.........lb.	.35	.35	.35
Oxide, bbls..............lb.	.07	.07	.08

*Resale or Imported (not an American makers' price).

ORGANIC CHEMICALS

	Sept. 1	Sept. 15	Jan. 1922
Acetanilide, U. S. P. bbls.......lb.	*.29	*.29	*.29
Acid, Acetic, 28 p. c.......100 lbs.	2.67½	2.67½	2.37½
Glacial..............lb.	.11	.11	.10
Benzoic, U. S. P........lb.	.55	.55	.60
Carbolic, cryst., U. S. P., drs................lb.	.20	.22	.12
50- to 110-lb. tins....lb.	.24	.24	.18
Citric, crystals, kegs......lb.	*.44½	*.45	*.43
Oxalic, cryst., bbls., wks...lb.	.17	.17	.14
Pyrogallic, resublimed....lb.	1.60	1.60	1.75
Salicylic, U. S. P.........lb.	.29	.29	.24
Tannic, U. S. P., bbls....lb.	.70	.70	.75
Tartaric, cryst., U. S. P...lb.	*.28½	*.30	*.25
Acetone, drums..............lb.	.13½	.16	.12
Alcohol, denatured, complete.gal.	.31	.31	.45
Ethyl, 190 proof, bbls....gal.	4.65	4.65	4.75
Amyl Acetate...............gal.	2.00	2.00	2.00
Camphor, Jap, refined, cases...lb.	.83	.83	.90
Carbon Bisulfide, c/l.........lb.	.06	.06	.06½
Tetrachloride............lb.	.10	.10	.10½
Chloroform, U. S. P., drums...lb.	.25	.25	.43
Creosote, U. S. P.............lb.	.40	.40	.40
Cresol, U. S. P...............lb.	.14	.14	.14
Dextrin, corn...........100 lbs.	3.09	3.09	2.70
Imported Potato.........lb.	.09	.09	.06½
Ether, U. S. P., 100 lbs........lb.	.14	.14	.14
Formaldehyde, bbls...........lb.	.08	.10	.10½
Glycerol, dynamite, drums....lb.	.15	.15	.14½
Methanol, pure, bbls.........gal.	.72	.80	.75
Methylene Blue, med.........lb.	3.00	3.00	4.00
Petrolatum, light amber......lb.	.04½	.04½	.05¼
Pyridine....................gal.	1.75	1.75	1.75
Starch, corn, pow'd......100 lbs.	2.47	2.47	2.13
Potato, Jap..............lb.	.07	.07	.06½
Sago......................lb.	.03½	.03½	.04



Courtesy of Drug & Chemical Markets

OILS, WAXES, ETC.

	Sept. 1	Sept. 15	Jan. 1922
Beeswax, pure white . . . . lb.	.40	.40	.33
Castor Oil, No. 3..............lb.	.12	.12	.10½
Ceresin, yellow . . . . lb.	.08	.08	.07½
Corn Oil, crude, tanks, mills...lb.	.09½	.09½	.06¾
Cottonseed Oil, crude, f. o. b. mill . . . . lb.	.08½	.08½	.07
Linseed Oil, raw c/l . . . . gal.	.88	.90	.69
Menhaden Oil, crude, mills.. gal.	.40	.41	.35
Neat's-foot Oil, 20°...........lb.	.20	.20	.16¾
Paraffin, 128–130 m. p., ref.....lb.	.03¾	.03¾	.05
Rosin, "F" grade, 280 lbs....bbl.	6.30	6.30	5.30
Rosin Oil, first run ....gal.	.39	.40	.36
Shellac, T. N.................lb.	.70	.67	.66
Sperm Oil, bleached winter, 38°.......................gal.	1.35	1.35	1.70
Stearic Acid, double pressed...lb.	.09½	.09½	.09¾
Tallow Oil, acidless...........lb.	.10	.10	.10
Turpentine, spirits of....... gal.	1.23	1.30	.82½

METALS

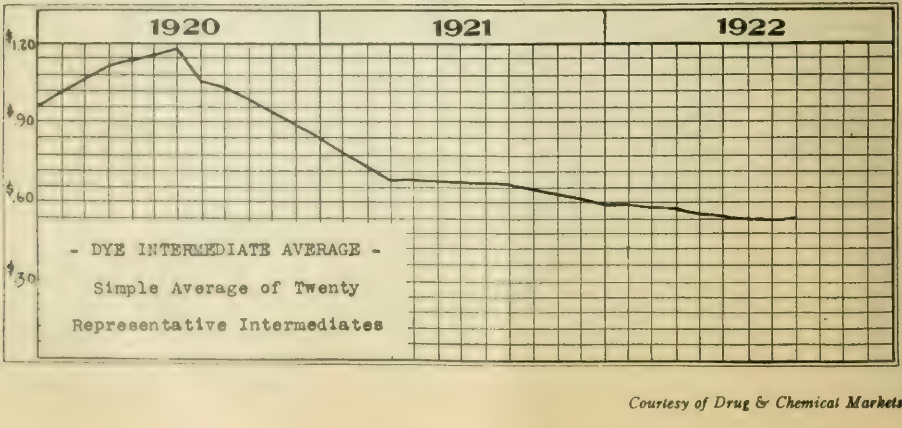
	Sept. 1	Sept. 15	Jan. 1922
Aluminium, No. 1, ingots.....lb.	.17½	.17½	.17
Antimony, ordinary......100 lbs.	5.25	6.50	4.55
Bismuth.....................lb.	2.10	2.20	1.80
Copper, electrolytic..........lb.	.14	.14	.13⅞
Lake..................lb.	.14	.14	.13¾
Lead, N. Y..............100 lbs.	5.75	6.05	4.70
Nickel, electrolytic...........lb.	.39	.36	.45
Platinum, refined, soft........oz.	93.00	118.00	78.00
Quicksilver, flask......75 lbs. ea.	62.00	66.00	52.00
Silver, foreign...............oz.	.71⅝	.69	.65¼
Tin.........................lb.	.32	.32	.32¾
Tungsten Wolframite....per unit	3.00	3.25	2.00
Zinc, N. Y..............100 lbs.	6.25	6.60	5.20

FERTILIZER MATERIALS

	Sept. 1	Sept. 15	Jan. 1922
Ammonium Sulfate, expt..100 lbs.	3.50	3.50	2.60
Blood, dried, f. o. b. N. Y....unit	4.00	4.00	3.50
Bone, 3 and 50, ground, raw..ton	28.00	28.00	30.00
Calcium Cyanamide, unit of ammonia	2.75	2.75	2.25
Fish Scrap, dried, wks......unit	4.10 & .10	4.10 & .10	3.25 & .10
Phosphate Rock, f. o. b. mine:			
Florida Pebble, 68%.....ton	3.00	3.00	5.00
Tennessee, 78–80%......ton	4.00	4.00	8.00
Potassium Muriate, 80%....unit	.60	.60	*.75
Tankage, high-grade, f. o. b. Chicago...............unit	4.00 & .10	4.00 & .10	3.00 & .10

COAL-TAR CHEMICALS

	Sept. 1	Sept. 15	Jan. 1922
Crudes			
Anthracene, 80–85%.........lb.	.75	.75	.75
Benzene, pure, tanks ....gal.	.30	.30	.29
Naphthalene, flake...........lb.	.06½	.06½	.07½
Phenol, drums . . . . lb.	.18	.20	.11
Crudes *(concluded)*			
Toluene, pure, tanks.........gal.	.30	.30	.30
Xylene, 2 deg. dist. range, tanks..................gal.	.45	.45	.45
Intermediates			
Acids:			
Anthranilic..............lb.	1.10	1.10	1.10
Benzoic, tech............lb.	.50	.50	.50
Cleve's..................lb.	1.50	1.50	1.50
Gamma...................lb.	1.80	1.80	2.25
H........................lb.	.75	.75	1.00
Metanilic................lb.	1.00	1.00	1.60
Monosulfonic F..........lb.	2.30	2.30	2.30
Naphthionic, crude.......lb.	.60	.60	.65
Nevile & Winther's.......lb.	1.20	1.20	1.30
Picric...................lb.	.20	.20	.25
Sulfanilic................lb.	.22	.22	.26
Tobias'..................lb.	1.50	1.50	2.00
Aminoazobenzene............lb.	1.15	1.15	1.15
Aniline Oil..................lb.	.14	.14	.17
Aniline Salt.................lb.	.20	.20	.25
Anthraquinone (sublimed)....lb.	1.35	1.35	1.50
Benzaldehyde, tech...........lb.	.65	.65	.45
U. S. P..................lb.	1.40	1.40	1.25
Benzidine Base..............lb.	.85	.85	.90
Benzidine Sulfate............lb.	.70	.70	.70
Diaminophenol..............lb.	5.50	5.50	5.50
Dianisidine..................lb.	4.50	4.50	4.75
p-Dichlorobenzene...........lb.	.17	.17	.15
Diethylaniline...............lb.	.60	.60	.90
Dimethylaniline..............lb.	.32	.32	.40
Dinitrobenzene..............lb.	.20	.20	.21
Dinitrotoluene...............lb.	.20	.20	.25
Diphenylamine..............lb.	.58	.58	.58
G Salt......................lb.	.65	.65	.70
Hydroquinol.................lb.	.80	1.15	1.35
Monochlorobenzene..........lb.	.10	.10	.10
Monoethylaniline............lb.	1.00	1.00	1.00
b-Naphthol, dist.............lb.	.22	.22	.30
a-Naphthylamine...........lb.	.30	.30	.30
b-Naphthylamine...........lb.	.95	.95	1.05
m-Nitroaniline..............lb.	.72	.72	.85
p-Nitroaniline..............lb.	.75	.75	.77
Nitrobenzene (Oil Mirbane)...lb.	.10	.10	.10
p-Nitrophenol...............lb.	.75	.75	.75
o-Nitrotoluene..............lb.	.12	.12	.15
p-Nitrotoluene..............lb.	.60	.60	.70
m-Phenylenediamine.........lb.	1.00	1.00	1.10
p-Phenylenediamine..........lb.	1.50	1.50	1.60
Phthalic Anhydride..........lb.	.35	.35	.38
R Salt......................lb.	.55	.50	.60
Resorcinol, tech.............lb.	1.30	1.30	1.50
U. S. P..................lb.	1.75	2.00	2.00
Schaeffer's Salt. ....lb.	.60	.60	.70
Sodium Naphthionate........lb.	.60	.60	.70
Thiocarbanilide..............lb.	.35	.35	.40
Tolidine (base)..............lb.	1.15	1.15	1.20
Toluidine, mixed............lb.	.30	.30	.30
o-Toluidine.................lb.	.16	.16	.20
p-Toluidine.................lb.	1.00	1.00	1.10
m-Toluylenediamine.........lb.	.95	.95	1.10
Xylidine.....................lb.	.42	.42	.40



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EDITORIALS

Authors' Synopses

OUR idea of having synopses precede the longer articles appearing in THIS JOURNAL has been approved at home and abroad. The next step is to improve them, and this we believe can best be done by the authors themselves. Even an expert abstractor often fails to emphasize the points the author particularly desires to have stressed. In order that our readers may gain an adequate idea of the scope of the article, authors are urged to prepare their own synopses, using as a guide those that have proved of greatest assistance in their own reading. Such synopses will serve to give a true impression of the author's work to the men who cannot afford the time to read in their entirety the many discussions in the chemical literature of to-day.

Chemists to Supply Facts

DURING the last few years chemists have been impressed with the incredulity of the average man, who simply cannot believe the things the chemist says are done through the science. Imagine a man who knew nothing of the telephone being told that by speaking into a receiver his voice could be heard three thousand miles away. Very likely he would not believe it, but it could be demonstrated much more easily than some of the facts peculiar to chemistry. We have a complex subject difficult to explain to any nontechnical man. Yet we have never failed to convert such a man to chemistry when once he really understood and was given a glimpse of its possibilities.

Out of this experience has come the suggestion that in each congressional district reputable chemists shall be designated to present chemistry in its true light to their representatives. Senators and Congressmen are to be given personal information, not with reference to party or any past or prospective legislation, but simply to make sure that they are conversant with the work of the chemist—his aims and his relation to the community. The effort is wholly nonpolitical and has for its primary purpose the establishment of a source of reliable nonpartisan and unprejudiced information. As a result of these personal contacts and the confidence thus gained, it is reasonable to suppose that when chemical questions arise and these public men are called upon to express an opinion on a measure, they will instinctively turn for information to the chemists whom they have thus come to know.

It is also suggested that when members of the SOCIETY are in Washington they call upon Secretary Parsons in order to learn if members of Congress desire information which they can furnish through a personal call. We have been impressed with the effort made by men in public life to sift the chaff from the wheat in the mass of material sent them, in order to obtain accurate information to guide them in their actions. It is not surprising that with the pressure brought from all quarters this has proved a difficult task.

All this is a part of an ambitious program which becomes a highly constructive piece of work if supported as it should be by our Local Sections and individual members. Let us take up the work now, carry it through with persistence, and convince the public of the importance of chemistry in its daily life.

Why Not Seek Advice?

THE DAILY PRESS has devoted much space to the discussion of reparation dyes as a possible partial payment of our bill for maintaining the Army of Occupation. It now becomes apparent that the plan has many flaws and that the news item was not based on facts. The State Department has admitted the necessity of special legislation to legalize such a plan, and it is doubtful whether such legislation could be secured. The plan involves securing the dyes and chemicals, importing them, and distributing them. These steps would require an organization which the State Department does not possess, and would make it necessary to call in many specialists. It is no small task to know what colors are wanted and who wants them, and when the various details of dyestuff importation are considered it looks more and more like a poor piece of business for the Government.

It seems probable that the State Department, without careful examination, thought that in the chemical situation it had an excellent opportunity to obtain considerable credits against the bills rendered. As a matter of fact, if such a plan were honestly administered and only those items that take foreign valuation were imported, the annual sum total would be but a small fraction of the interest upon our bill. These materials would be subject to duty, and a business transaction would be involved of a character doubtful from the standpoint of government.

Apparently chemistry is the ready-made pawn in the international game to-day—a key to improved conditions abroad in that the United States has no representative on the Reparations Commission. Through the chemical situation there may be an opportunity to wield the influence which many believe the United States should exert. But does that justify the embarrassment which has been caused the industry even temporarily? We think not. All the facts were and are accessible. Why was not expert advice sought when it could be had for the asking?

Service to Sections

THERE are two ways in which we could be of service to Local Sections, but in both we are helpless unless the Sections coöperate with us.

First, we have many requests for advance information as to time and place of Local Section meetings and names of speakers. A few Sections plan a year's program around some definite idea, secure their speakers in advance, and give publicity to their program. Obviously, this is not always possible, but much good would doubtless be accomplished if secretaries would have this idea in mind in planning their programs. Programs of Local Sections should be printed for the benefit of members generally, and especially for those who may be away from home and who would be glad to attend a meeting if they knew of it. The News Service can give publicity to Local Section meetings only when information is received considerably in advance. The publication of meeting papers can also be planned to better advantage if we are notified in advance of their presentation and nature.

Your assistance is also needed in the routing of speakers. It frequently happens that a Section engages a speaker to come from a considerable distance. Doubtless other Sections in the same vicinity or en route would like to have the same man address them if they knew that he was in their general locality. If, therefore, you will let us know your plans, we will broadcast them immediately. The net result should be the conservation of the speaker's time, prorating of expenses between Sections, and, in some cases, decided improvement of the program.

Current Literature Located

IT IS a common experience for an investigator to need a journal containing a paper of interest without knowing just where to turn to obtain it. Even the commonest journals are not readily available to all, and the rarer ones are to be found in only a few places. Hardly a mail is received in the office of *Chemical Abstracts* that does not contain one or more letters of inquiry as to how a paper corresponding to an abstract can be procured. A means that furnishes ready answers for the chemist to this frequent problem has now been provided in the form of journal location data for libraries scattered throughout the United States.

The "List of Periodicals Abstracted by *Chemical Abstracts*" has been brought up to date and published in the October 20 number of the abstract journal. In addition to the information formerly given in this compilation, it is now stated, for each periodical, which of 172 of the principal libraries of the United States currently receive it, and for each library it is stated whether it conducts a lending, photostat, or translating service. Since the list of periodicals is a comprehensive one as far as journals of chemical interest are concerned (it contains more than a thousand entries), this means that the chemist can now readily determine in almost every case of need just where the nearest available copy of a journal is to be found. If it is not feasible to go to the journal file, he can usually obtain a photostat copy of the paper needed or obtain the journal as a loan.

If one wishes to subscribe for a journal or to buy a single current number, he will find in the list the names and addresses of the publishers of the various journals, and usually the domestic and foreign prices for single numbers and for a year's subscription. It is to be noted that the prices of German journals have been constantly increasing since the World War. Many of them seem much too high. Sometimes after a subscription is entered for a definite period, as a year, and payment accepted, the price will be raised and additional payment demanded—a practice difficult to reconcile with American business methods.

Librarians, who responded in a fine way to the appeal for coöperation in the compilation of this information, are an accommodating crowd. Our gratitude is due them for their fine spirit of service. Their willingness to coöperate in the preparation of the location data signifies their readiness to help those who will use these data.

In the revision of the list the abstractors have coöperated on all journals not available in Columbus. At the suggestion of the editor of *The Journal of Industrial and Engineering Chemistry*, and by his arrangement, the canvass of libraries was accomplished by the Research Information Service of the National Research Council. Clarence J. West and Callie Hull conducted it in a very effective manner.

We shall be glad to be told of additional journals of chemical interest which should be made a part of the list. Completeness has been especially sought. Corrections will also be welcome. It is our plan to publish a revised list with up-to-date library information in about two years. Reprints of the list will be available at cost price.

E. J. Crane

Industrial Alcohol Situation

SINCE the enactment of the National Prohibition Act, governmental conditions surrounding the manufacture, distribution, sale, and use of alcohol for industrial purposes have become so increasingly onerous as seriously to handicap the chemical industry.

Title III of the National Prohibition Act provides not only for the manufacture, distribution, sale, and use of *industrial alcohol*, as distinguished from potable intoxicating liquors, but for the *development* of lawful industries that use alcohol as a raw material.

A former Commissioner of Internal Revenue created the office of Federal Prohibition Commissioner, the incumbents of which have since undertaken to enforce both the *prohibitory* and *permissive* features of the law, through a specially organized staff of prohibition enforcement officers, under a complicated system of regulations. No provision was made for an industrial alcohol administrator to enforce, apart from, but in coöperation with, a prohibition officer, the provisions of Title III regarding industrial alcohol lawfully withdrawn in the form of tax-free or tax-paid ethyl alcohol or denatured alcohol. On the contrary, a governmental policy was adopted of trying to scramble the enforcement of prohibition and the administration of the legitimate uses of industrial alcohol into one political organization. The result has been a signal failure, at least with respect to industrial alcohol.

The intention of Congress to separate the administration of industrial alcohol from prohibition enforcement is implied in the act itself by Titles II and III. The action of a Commissioner of Internal Revenue, therefore, in vesting in a prohibition enforcement organization without the essential technical and economic knowledge and training, the duty of carrying out the provisions of Title III, was illegal by implication, illogical by any method of sound reasoning, economically impractical, and should be changed. In order that the legitimate uses of alcohol may not be further hampered and curtailed, we deem it proper to suggest a prompt change of the present procedure along the following lines, *which will not entail any modification of existing law:*

(1) The Commissoner of Internal Revenue should immediately designate a Deputy Commissioner of Internal Revenue, or an Industrial Alcohol Commissioner, to take over the administration of that portion of the law relating to industrial alcohol. The regular Collectors of Internal Revenue and Civil Service revenue officers should be designated to assist him as is customary in the enforcement of other internal revenue laws. The Deputy or Industrial Alcohol Commissioner should possess suitable technical knowledge, training, and experience to place the nonbeverage alcohol industry and other industries using such alcohol upon the highest possible plane of scientific and commercial efficiency.

It would be the duty of the Deputy or Industrial Alcohol Commissioner to issue basic permits to withdraw and use industrial alcohol of any kind. In this way efficient and scientific administration would be assured, and at the same time the Prohibition Commissioner or Attorney General would be relieved from supervision of legitimate industry and could devote his energy to his proper duty of *policing* the situation. Furthermore, the two agencies, coördinating, would be a check upon each other.

(2) The Commissioner of Internal Revenue should invite the active support and assistance of an advisory committee of technical and commercial experts to assist the industrial alcohol unit in investigating all applications for permits and furthering the uses of industrial alcohol in scientific research.

(3) Scientific study and research should be encouraged by the establishment of a properly equipped laboratory distinct from policing laboratories and devoted exclusively to alcohol problems. This would unquestionably result in the development and improvement of denaturation, evolution of new denaturants, perfection of formulas required by specific industries, etc., and would seem to be a logical and sound step in unfolding the prohibition enforcement program along the lines that will not interfere with industry. If it is not practicable to have such a government laboratory, then one should be built and subsidized by the civic, religious, and other bodies that are constantly appealing to the public for funds with which to aid the Government in enforcing the Eighteenth Amendment and the National Prohibition Act. Much can be said in favor of this last proposition. Such a privately endowed laboratory would occupy a neutral position between the chemical industry and the governmental prohibition enforcement program, and, by keeping abreast of the ingenious "bootlegger, "could furnish truly constructive assistance which would relieve lawful trade from unwarranted stigma without increasing the taxpayer's burden.

Alcohol is admittedly a basic chemical essential to our national defense, industrial and economic development, and even to the advancement of civilization itself. Therefore, all who believe in law enforcement should recognize the intolerable situation to which the chemical industry has been brought by failure to properly enforce the industrial alcohol features of the law, and should make certain that it is administered as intended by Congress.

The Chemist Versatile

HOW many of our chemists, particularly the younger men, have been trained as chemists and nothing more? During the discussion of the proposed dismissal of trained employees of the Bureau of Printing and Engraving, the argument was advanced that the men concerned were specialists and unable to earn a living in another field. How many in our profession are specialists to the same degree?

In times of industrial stress are the research men sufficiently resourceful to assist in finding a way out for their employers by advising new products and making helpful suggestions, or do they insist upon adhering to the scientific problem in hand under all conditions? At such times development work is often stopped and efforts concentrated upon goods that can be sold in the prevailing market. The thought of the versatile chemist is needed on the new set of problems then presented.

Chemists must be prepared to change with the times. We should be able to cultivate a minor vocation without detracting from our usefulness as chemists. The special training which we receive should fit us for many types of work, including that of the executive, in which we too seldom have an opportunity to demonstrate our abilities. Broad, fundamental training should make it possible for the chemist to fit in where needed, but he must not only know his subject but be able to express his ideas clearly on paper or verbally. He must know how to meet people. He must be familiar with business principles.

The younger men can form valuable contacts, take responsibility, and try themselves in a way that cannot fail to broaden them, in the activities of Local Sections of the SOCIETY. We have seen many men develop under the opportunities of active work in Local Sections and can recommend it. It is, of course, incumbent upon the older men in the Sections to make sectional enterprises attractive to the younger men, to make a way for them to be active, and to counsel them in their work. This can be done without entrusting the future progress of the Section entirely to untrained hands.

There are as many varied opportunities for constructive work by the chemist in the body politic as for the corpuscles of the blood in the human body.

The Earning Power of Research

THE advantage of coöperation between chemists and other scientists has often been stressed. The examples of profitable results from such coöperation may not be so familiar.

Paleontology might not be considered an ally of chemistry, and yet we find that certain fundamental researches carried on years ago have now become of the utmost importance in locating oil sands leading to the discovery of commercial fields and the expansion of the petroleum industry, which is so largely chemical. The groups of organisms studied have exceedingly interesting habits and highly artistic forms, but none of them are of industrial or commercial importance. They do not yield food, or minerals, or gums, or waxes, but are small enough so that their fossils are to be found in samples from a boring and escape destruction by the drills. One group constitutes almost the only fossils in the thick series of calcareous clays that overlie the oil sands in the Tampico district.

Edward W. Berry of Johns Hopkins, in discussing this subject in *Science* for December 3, 1920, states that "in the Tampico district alone the knowledge that has been gained from the study of these ancient fossils will eventually contribute more in dollars and cents to the wealth of the world than all of the issues of the *Congressional Record* that have ever been printed." He concludes:

> "The ultimate commercial value of these monographic paleontologic studies that are published by the National Museum—the exploration for oil in central and northern South America, and the successful interpretation of structure that is the key to commercial success or failure in the far off *tierra caliente* of Columbia or Venezuela—rests very largely on the application of the results of the unostentatious and unadvertised paleontologic studies."

IN New England a certain manufacturer was paying a high price for a special paper in the belief that price was an index of the particular quality required in his electrical work. Research upon actual requirements revealed the fact that a less expensive paper was better and that carefully drawn specifications would secure a satisfactory material at a saving which made a thousand per cent a year on the investment in research.

Spilled Milk

FAR-SIGHTED men generally have decried the willingness of many corporations to separate from their service trained scientists with years of experience in their specialty at the first indications of the passing of soft times. It is interesting to note now that some of these corporations, finding business improving, seek to rebuild a scientific staff. They find their former specialists employed elsewhere and themselves with such a reputation as a result of their recent action that the men whom they would like find nothing attractive in their offers. We trust the lesson will be well remembered in the future.

AUTOMATIC PROCESS CONTROL SYMPOSIUM

Papers presented before the Division of Industrial and Engineering Chemistry at the 64th Meeting of the American Chemical Society, Pittsburgh, Pa., September 4 to 8, 1922

Control of Industrial Heating Processes

By J. A. Doyle

W. S. Rockwell Co., 50 Church St., New York, N. Y.

THE INFLUENCE of heat upon the quality and cost of nearly all manufactured products, and the comparatively inefficient methods of heating and handling in general use, suggest the necessity for a better understanding of the factors that govern the production of heat-treated products and the possibility of controlling the many variable elements affecting the selection and use of equipment and fuel for their production.

QUALITY AND COST OF PRODUCT

Quality and cost of finished product should be considered as the basic factors affecting the conduct of industrial heating operations. There are many contributing factors, including the influence of the human element and intangible values which cannot be definitely measured, outlined in Fig. 1,[1] any one of which may affect the ultimate result.

Control of furnace temperature is generally considered the most essential factor affecting the quality of a heat-treated product, and the price or consumption of fuel or electricity as the dominant factor affecting the cost of the product. This view, while unfortunately more or less prevalent throughout the industry, is nevertheless unsound, as the development of the art following demand for better and cheaper products has proved.

The problem of control with reference to quality involves control of the supply of fuel or electricity to the furnace, control of supply of heat to the working chamber, control of the flow of heat as it is actually applied to the surface of the product, control of the atmosphere surrounding the product, and control of the time of exposure and the rate at which the heat is transferred.

Control of the cost of finished product involves consideration of factors affecting the rate of production per unit of time, floor space, operative, fuel, etc., which is largely governed by the methods and equipment employed for heating, handling, and cooling the material to be heat-treated, and factors governing the cost of operation, which include not merely the price but the amount of fuel or electricity employed, labor, power, and other items that may be properly charged against operating cost.

COMMON FALLACY

It is a common but misleading assumption that control of chamber temperature or of supply of heat energy to a fur-

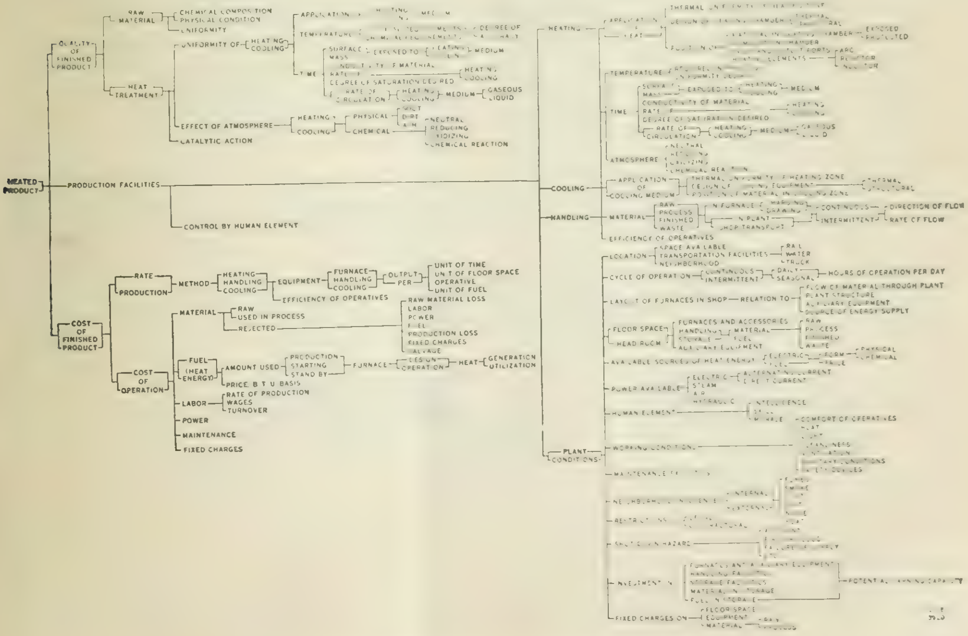

FIG. 1—FACTORS GOVERNING PRODUCTION OF HEATED PRODUCTS

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[1] Illustrations published with permission of W. S. Rockwell Company.

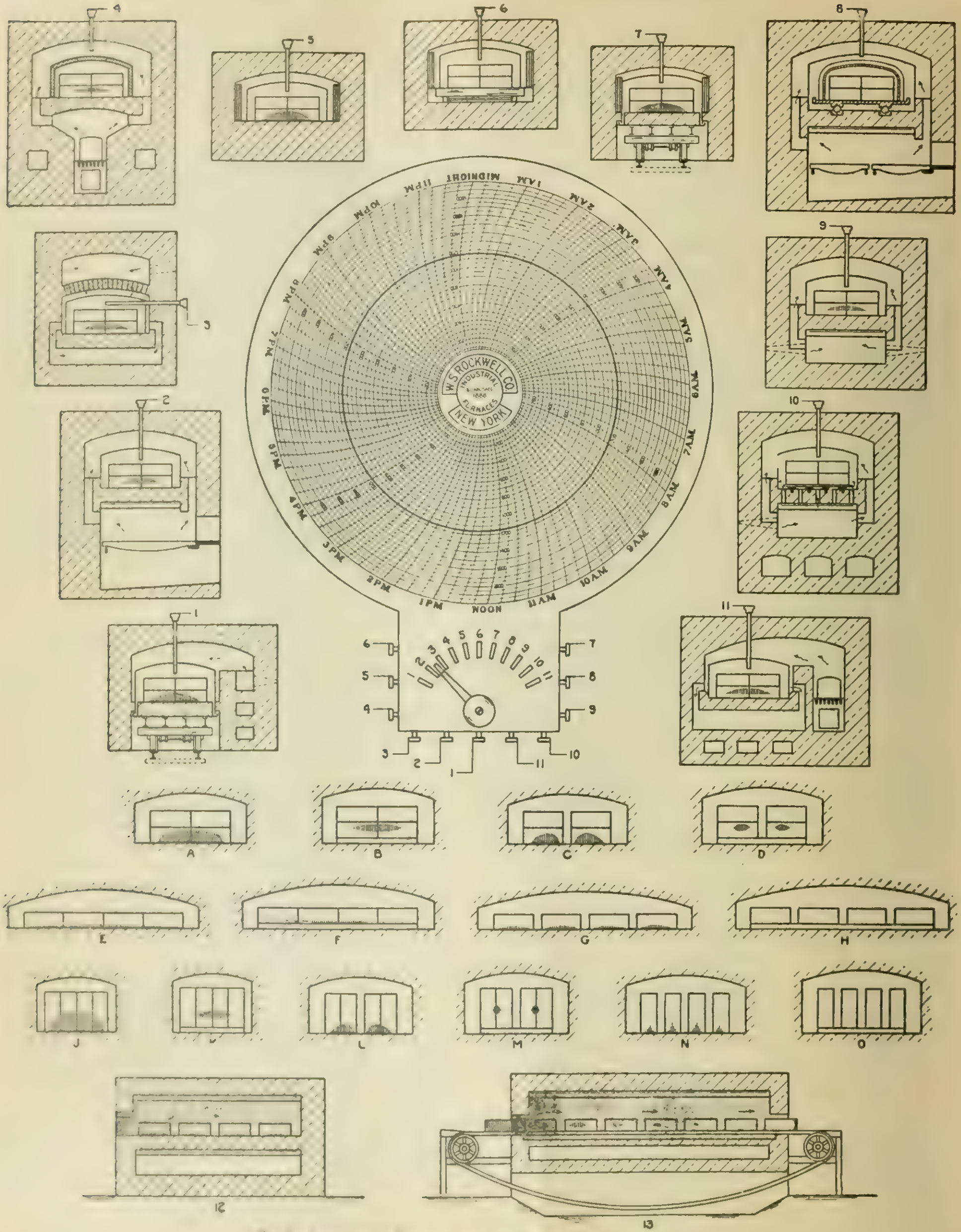

Fig. 2—Relation of Temperature Indication to Heated Product

heat is synonymous with control of the temperature of the heat-treated product. However, control of the generation of heat is not equivalent to control of the application of heat, or to control of the uniformity with which the product is heated or cooled.

The difference between control of heat as it is generated in the furnace and control of heat as it is applied to or transferred from the surface of the product is not generally realized.

Automatic devices set in motion by movement in the pyrometer are available for control of delivery of coal through stokers or in powdered form; of gas, oil, or steam through automatic valves; and of electricity through various forms of regulating devices—all of which may result in control of the manner of generating heat in a furnace, but do not necessarily control the application of heat to the product within that furnace.

Indication of temperature control is frequently accepted as evidence of control of the manner in which the product is heated or cooled, regardless of the fact that indication of uniform temperature does not of itself establish the uniformity of a heating or cooling process.

Uniform chamber temperature is necessary to produce a product that is uniformly heated or cooled, but heating a chamber uniformly and uniformly heating or cooling a charge within that chamber are distinct matters.

Of primary importance are the manner of heat application to the surface of the individual piece, the time of exposure, the rate of heating, and the composition of the heating or cooling atmosphere. Variation in product may result from difference in furnace design, in manner of placing the charge in the chamber, in the time of exposure, in the rate of heating, or the rate of charging and discharging, which may result in difference in manner of heat application or heat transfer without any indication by the pyrometer of temperature variation within the chamber.

The ideal condition for the production of properly treated product is approached when the heating and cooling mediums are uniformly applied to the entire surface of each section or piece, individually, in the same manner, at the same temperature, at the same rate, for the same time, in the same atmosphere, in equipment properly adapted to the nature of the process, form of fuel, or electricity employed, manufacturing requirements and plant conditions.

The relation of indicated chamber temperature to heated product is illustrated by Fig. 2.

The pyrometer chart is an accurate reproduction of one of a set, practically identical in character, indicating the temperature control in five furnaces operating on the same 24-hr. day. Although it might be assumed that a charge would be uniformly heated in any furnace recording such a chart, there would, nevertheless, be a marked variation in the uniformity with which the charge would be heated in some of the different types of furnaces (1 to 11), even though the indicated chamber temperature and the time of heating were the same in each case.

The approximate locations of the incompletely heated zones, reflecting a difference in furnace design or manner of loading, are shown by the shaded sections. The electric furnaces (5, 6, 7) are not exceptions to the rule, for while they may be alike in manner of generating and controlling the input of heat, they differ, like the various fuel-fired furnaces, in manner of applying the heat to the surface of the charge in the chamber.

The product may likewise vary in uniformity in each of these furnaces, depending upon the manner of distributing the charge (A to O) and of the mass and surface exposed to the heat, although there may be no variation of indicated chamber temperature or time of heating.

THE TIME-TEMPERATURE FACTOR

Unwarranted emphasis on *temperature control* as the essential element in heating or cooling operations, and on *output*, *fuel consumption*, etc., as the determining factors in cost, frequently leads to neglect of the influence of the time, manner of exposure, and the rate of heating or cooling upon the quality and cost of the finished product.

Control of time and rate of heating or cooling is just as essential as control of temperature. Time and temperature are so inseparably linked that it would be well to associate the two as one factor *time-temperature*. The use of such a term may tend to discourage the usual abstract consideration of temperature without regard to the time necessary to attain a given temperature, and to encourage the thought that there are a number of factors, subject to control in addition to temperature, that affect the uniformity with which a given product is heated or cooled.

Temperature is a more or less fixed factor, determined by the nature of the process and the physical or chemical requirements in the product to be heated or cooled. It should be considered with reference to the distinction between temperature of the chamber in which the product is exposed and the temperature throughout the product itself, which is naturally affected by the time of exposure and the rate of heat absorption.

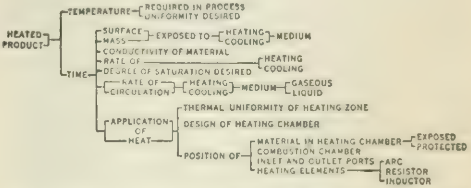

FIG. 3—FACTORS DETERMINING UNIFORMITY OF HEATING AND COOLING

Time of heating is a variable factor and is influenced by the manner of transferring heat to or from the surface of the product, the manner of loading or exposure, the relation of one piece to another and to the source of heat, the difference between temperature of the product and the chamber in which it is exposed, the rate of circulation over the surface, conductivity of the material of which the product is composed, relation of the mass of the charge to the chamber in which it is exposed, and other factors outlined by Fig. 3.

The rate of heating or cooling should be determined with reference to the physical or chemical requirements in the finished product, and to the mass, shape, section, exposed surface, and manner of exposure. The viewpoint of the engineer with reference to "the rate at which heat *can* be transferred" to save time or fuel, or to increase production, should be considered with the view of the chemist in determining "the rate at which heat *should* be transferred," in order to effect the desired result in quality of finished product.

The influence of variable section, shape, or surface exposed, upon the rate of heating or cooling may necessitate slow heating or preheating, in order that the mass may be well saturated before it is subjected to the final temperature. Disregard of this point is the cause of difficulties that frequently follow the practice of maintaining furnace temperature materially higher than that required in the product, in order to gain time or save fuel.

Control of temperature in a furnace is a function of the control of the input of heating energy, whether it be fuel or electricity; but there is a difference between that and control of the application of heat to the product.

The manner in which heat is applied to the surface of the product to be heated, which very largely reflects the design and method of loading and operating the furnace, is of paramount importance, and necessarily involves factors affecting the time of exposure and rate of heating and cooling, which are equally as important as factors that influence control of chamber temperature—all of which must be considered in order to produce a product as uniform as the pyrometer indicates it should be.

It is much more difficult to automatically control the variable factors affecting time and rate of heating or cooling than to control the factors affecting temperature, except in continuous furnaces, the use of which is limited to conditions that permit a steady flow of material uniform in character.

THE HUMAN ELEMENT

The great variety of chemicals subjected to the action of heat in the process of production, and the still greater variety in plant conditions requiring the use of different types of furnaces and forms of fuel or electricity, and the ever-changing methods resulting from development of the art make it difficult to indicate how these variable factors may be controlled without dependence upon the *human element* in the conduct of such operations.

The human element cannot be eliminated by automatic devices to control temperature, except in rare cases where the manufacturing routine does not vary in essential detail. Variations in size, shape, weight, quantity, rate of flow, time of exposure, rate of heating, composition of material, or nature of the heating or cooling process, call for the exercise of skill and judgment on the part of the furnace operative, in order that the charge may be properly placed and heated. As long as the many variable factors governing production of heat-treated products call for the exercise of judgment, just so long will the human element be the ultimate controlling factor. The need of the moment is for operatives or supervisors qualified to understand and properly apply the principles that govern correct heating.

It is in order to suggest, in view of the ever-increasing demand for better and cheaper products, that it is advisable for those concerned with the conduct of industrial heating operations to consider the importance of these variable factors and intangible values, and the simple principles affecting their control, because of their bearing upon the result sought in the form of finished product.

The needs of the future can only be met with better methods of heating and handling, better equipment, and, above all, men properly qualified to select and use the equipment that is such an essential part of the means to the end.

Automatic Volumetric Analysis Carbon Monoxide Recorder

By Guy B. Taylor and Hugh S. Taylor

E. I. du Pont de Nemours & Co., Experimental Station,
Henry Clay, Del.

CHEMICAL industry has been singularly backward in encouraging the development of automatic devices for control of operations. It has preferred in most cases to spend its energies on the development of rapid analytical methods which, when carried out in the works control laboratory, interfere with production to the minimum extent. There are no doubt many cases where routine analyses might be made by machines instead of by men, furnishing results more cheaply and quickly, or even recording them continuously. Often such machines might be capable of actually performing work in the plant, resulting in considerable labor saving as well as tending toward uniformity and high quality of product.

Undoubtedly, gas analysis offers the simplest case for development of automatic analysis and control devices. On the other hand, manual gas analyses seem to be avoided by industrial chemists. The reason for this is that gases are much more difficult to collect, handle, transport, and work with in the laboratory than solids or liquids. The compositions of gases evolved in many industrial reactions are still quite unknown.

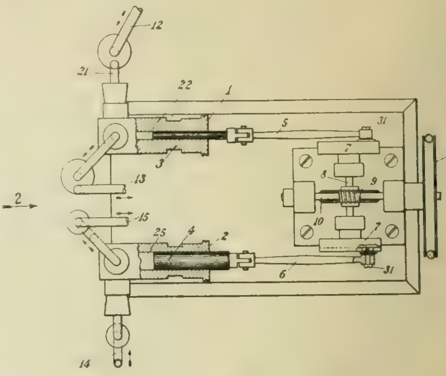

FIG. 1

Most, if not all, automatic-recording gas-analysis instruments on the market in the United States are designed specifically for carbon dioxide in flue gas. The principle upon which they all operate is to measure a quantity of the gas, absorb the carbon dioxide, and measure the unabsorbed residue. When this principle is applied to gases for constituents averaging 1 per cent of the total, obviously, obtaining the result by the method of differences of relatively large numbers may lead to serious errors. For example, a difference in temperature of 3° C. between the two measuring vessels of an instrument operating on the volume change principle, occurring after the instrument has been adjusted, would cause an error of 100 per cent in the record of the amount of constituent present at a concentration of 1 per cent.

In this paper we will describe an instrument adapted for direct determination of carbon monoxide or dioxide at low concentrations, but which is also applicable, when suitably modified, to other gases and other concentrations. In principle it consists of mixing continuously measured volumes of gas with a liquid reagent and measuring the resulting electrolytic conductivity change of the solution. The novelty

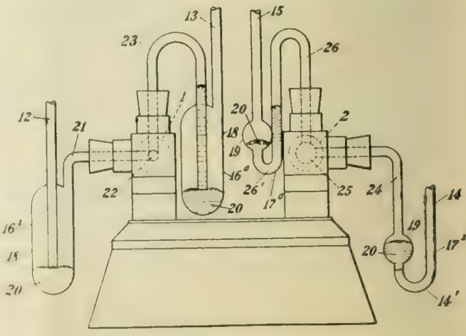

FIG. 2

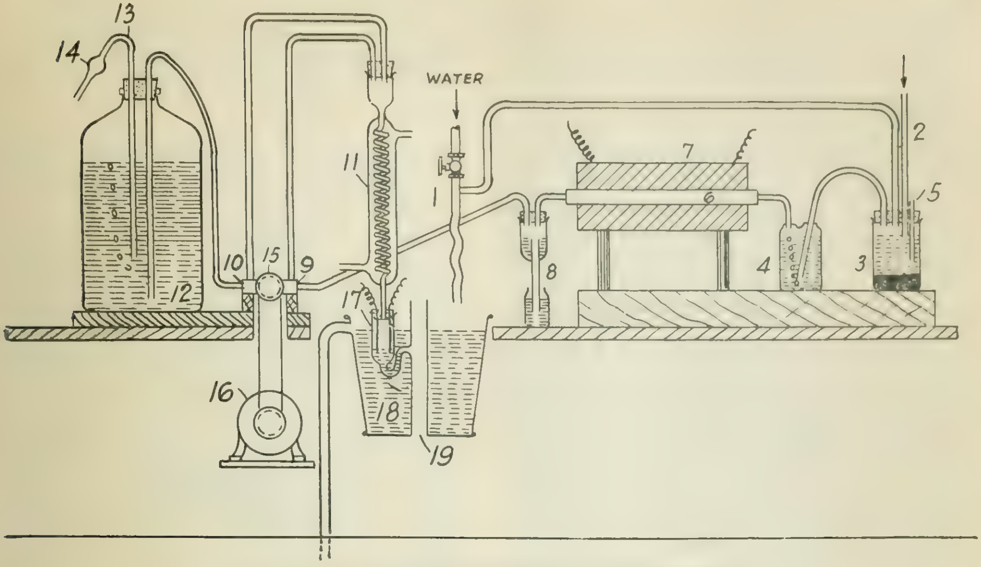

Fig. 3—Automatic Gas Analysis Apparatus for Carbon Monoxide

of the apparatus consists in the method of securing accurate control of the volume of the two fluids mixed. This method of mixing two or more fluids (gas and liquid, or liquid and liquid) makes it possible to make and record continuously any volumetric chemical analysis, if the resultant chemical or physical change can be recorded automatically. Among the chemical and physical changes which may be so recorded are electrolytic conductivity, hydrogen-ion concentration, temperature, density, thermal conductivity, etc.

E. K. Rideal and H. S. Taylor[1] published the first account of gas analysis on the electrolytic principle. Their apparatus was designed for the determination of traces of carbon monoxide in hydrogen. The gas was passed over a preferential oxidation catalyst which converted carbon monoxide to the dioxide. The gas stream then met standard limewater in a glass tower packed with glass wool. The less concentrated limewater then flowed to an electrolytic cell, the electrodes of which were connected with a source of e. m. f. and a recording milammeter. K. von Haken[2] developed a similar apparatus for carbon dioxide in flue gas.

The accuracy of this type of apparatus obviously depends upon maintaining a constant ratio of gas and reagent flow. In the Rideal and Taylor apparatus, liquid was delivered through a capillary under a constant head and the gas flow controlled by a capillary flowmeter. Von Haken controlled his flows by acomplicated system of manometers and floats. These methods may be satisfactory for short periods and for clean dry gas. For most industrial gases, variation in pressure at the point of sampling and dust in the gas make them inapplicable.

The ratio device developed by us consists of two piston pumps driven from a common shaft and thus stroking together. One pump delivers gas and the other, reagent. The volume ratio of the two is independent of variations in the speed of pumping. Piston pumps require valves, and in this case valves that never fail in their action and never slip. Mechanically closing valves of the ordinary types cannot be depended upon, especially when the bore of the pump cylinder is only a small fraction of an inch in diameter. This difficulty was overcome by the use of mercury traps as valves (Figs. 1 and 2).

Description of Carbon Monoxide Recorder

The recorder described below was developed for the control of a gas-fired furnace.

Fig. 3 is a diagrammatic sketch of the original apparatus, which may be used to illustrate the working of the instrument. Gas from the furnace is aspirated by 1 and enters through pipe 2, which just dips under water in bottle 3. A continuous rapid bubbling is maintained. Pipe 5 is a safety tube where air may enter if any obstruction occurs in the line to the furnace. A portion of the gas drawn from the furnace bubbles through potassium hydroxide in 4 to absorb carbon dioxide. Carbon monoxide is burned to dioxide by hot copper oxide in quartz tube 6, heated by electric furnace 7. Device 8 contains concentrated sulfuric acid for partial drying of the gas to avoid condensation of water in the pump and valve trap. The ratio pumps are indicated in the figure by 9 and 10; 15 is the pulley wheel on the gear reduction operating the pumps, and 16 an electric motor. Tenth normal ammonium hydroxide in 12 is pumped to spiral 11 and there meets gas pumped by 9. In flowing down the glass spiral, carbon dioxide is absorbed, which absorption increases the conductivity of the ammonia solution directly proportional to the amount absorbed. This solution runs through cell 17 and wastes through 19. Water in bucket 18 maintains the cell at a fairly constant temperature, and is supplied continuously by aspirator 1.

Ratio Pump—A plan and end elevation of the ratio mechanism are shown in Figs. 1 and 2. The bore of the solution pump is $^{3}/_{16}$ in. and that of the gas pump $^{1}/_{2}$ in. The pins 31 are movable along the diameter of the crank disk 7 for adjusting the length of stroke. The solution pump is adjusted to deliver 0.25 cc. and the gas pump 1.00 cc. per stroke. The pumps stroke 40 times per min. The valve traps on the gas side are made of capillary glass tubing (Fig. 2, 14–15) with bulbs about $^1/_2$ in. inside diameter. The solution traps are of different construction, as shown in the figure. Tubes 12 and 23 are capillaries, with ends which just dip below the mercury surface 20. The absorbing liquid completely fills the rest of the space in the two traps. The action of these traps will be clear from a glance at the drawing. The positions of the mercury columns shown in the figure are those at the end of the suction strokes. Solution and gas have entered the cylinders by bubbling through mercury seals 20 in 16*i* and 17*i*. In the traps 16*o* and 17*o* the mercury columns have risen and sealed the outlets. On the pressure stroke, these columns fall and corresponding columns seal the inlets while the cylinders are discharged.

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[1] *Analyst*, **44** (1918), 89.

[2] *Z angew. Chem.*, **33** (1920), 188.

Electrical Recording System—The cell is made from a filter tube of the size to hold a No. 7 rubber stopper. The electrodes are smooth platinum, 6 mm. square, spaced 13 mm. apart. The holes in a standard No. 7 two-holed stopper are spaced about right. These electrodes are connected in series with a recording milammeter, range 0 to 50 milamperes, and about 13 dry cells. The circuit is provided with a double-pole, double-throw, knife switch, so that either the cell or a standard 500 ohm resistance can be placed in circuit with the ammeter. With the coil in circuit enough batteries are used to make the ammeter read 38 to 40 milamperes—usually 13 new cells are necessary. If 13 gives too high an amperage and 12 too little, used cells remedy the difficulty. After adjusting the voltage to 19 or 20 volts by this method, the cell is put in circuit, and with 0.1 *N* ammonia at about 25° C., the reading should be 10 milammeters. If the gas-solution ratio is now 4 to 1, each increase of 5 milamperes above 10 will correspond to 1 per cent carbon monoxide. Each dry cell lasts about a month with continuous service. An adjustment by combination of old and new cells once a week is all that is required to maintain the proper voltage.

Performance and Precision

The apparatus as described will determine carbon monoxide in flue gas or in the air up to a total of 8 per cent, with an accuracy of ±0.2 per cent at temperatures around 25° C. With no temperature control on any part of the apparatus except the cell, the results should not be in error more than ±3 per cent of the amount present. The temperature coefficient of electrical conductivity being quite high, the cell must necessarily be placed in a bath. With tap water constantly running through the bath, the temperature variation from day to day is not serious but may be so from month to month. This is corrected by occasionally changing the gas-solution ratio. The original apparatus as made from ordinary laboratory equipment ran almost continuously for six months with no skilled attention. The furnace operator took almost complete care of the apparatus, being supplied daily by the laboratory with 5 gal. of 0.1 *N* ammonia. The method of making this solution was simply to add 130 cc. strong reagent ammonium hydroxide to 5 gal. of distilled water.

Since the original apparatus was built, two others have been constructed in much more compact form and placed in substantial wooden cabinets.

Applications

The recorder described is applicable generally for flue gas. Its sensitivity can be extended to the detection of the lower concentration of carbon monoxide encountered in mine air and in underground vehicular tunnels. Hydrocarbons of the methane series do not necessarily interfere, because carbon monoxide can be preferentially burned to carbon dioxide.

As mentioned above, use of the ratio device[3] is not restricted to gas analysis. Many other volumetric analyses, involving two or more fluids, might conceivably be performed with its aid.

Hydrogen-Ion and Other Electrical Measurements as Applied to Process Control

By Earl A. Keeler

Leeds & Northrup Co., Philadelphia, Pa

The increasing use of hydrogen-ion measurements in the industrial laboratory naturally leads one to a consideration of the possibilities existing for such methods in automatic process control. No other electrical measurement utilized in the chemical industries possesses such an extensive and varied field for application as that of the hydrogen ion. Related as it is to the activity, or actual acidity, of solutions, it has become a factor of great importance in the control of many chemical processes. The usual chemical titration is sometimes misleading because it measures total acidity or alkalinity, thus including both free acidity and that due to salts exhibiting an acid or alkaline reaction. The hydrogen-ion concentration, or actual acidity, is frequently the predominant factor entering into reaction control.

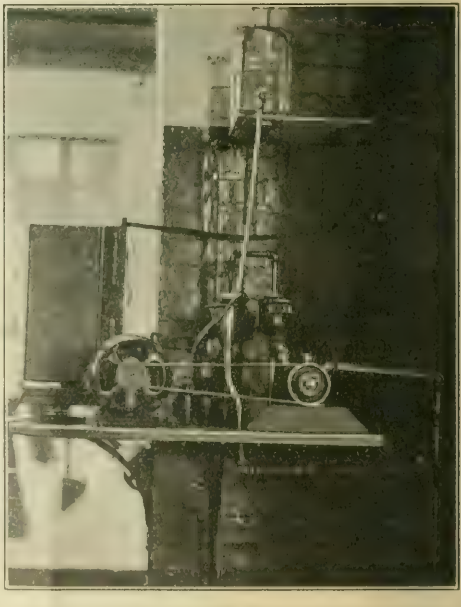

Fig. 1

The development of the hydrogen-ion automatic process control has been greatly retarded by the difficulty experienced in constructing electrode structures suitable for industrial application. Consequently, this paper is more of the nature of a statement of possibilities rather than a completed report of installations in operation. Considerable improvement has been made in the electrodes available, and efforts are now being made to apply hydrogen-ion control to the various processes encountered in the chemical industry. Up to the present time, most of the automatic control work has been along the line of maintaining a definite hydrogen-ion concentration of boiler feed. It is well known that one of the factors entering into the corrosion of boiler steel is the hydrogen-ion concentration of the boiler feed. By maintenance of the feed to a concentration corresponding to a slight alkalinity, the corrosion of the boiler and its auxiliaries may be materially reduced.

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[3] Patent applied for.

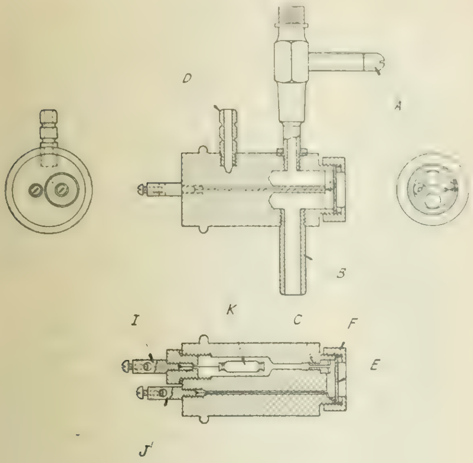

Fig. 2

Fig. 1 shows a hydrogen-ion recorder controller as installed for boiler feed control. Caustic soda is added to maintain a slight alkalinity. The water passes through a small filter and a simple air electrode operating on the aspirator principle.[1] Such an electrode is shown in section in Fig. 2. The automatic valve shown in Fig. 3 is motor-operated from the control circuits of the recorder controller, and opens or closes the caustic soda line leading to the feed water heaters. Another caustic soda line is by-passed around the automatic valve. This line continually feeds a small amount of alkali to take care of the minimum demand of the system. Variations of acidity or alkalinity result in the automatic valve opening or closing, thus altering the rate of alkali flow into the boiler feed. The tank and piping for handling the caustic soda solution are also shown in Fig. 3. The equipment described in this installation is practically the same as that required for various other applications of the hydrogen-ion automatic process control. A previous paper on this subject is of interest in that it is indicative of the possibilities existing for the application of automatic control to the chemical industry.[2]

Other types of automatic process control utilizing electrical measuring equipment have already proved successful. Among these may be mentioned the important stage of oil refining known as the "cracking" process. Here the temperature-recorder controller performs a useful duty in maintaining the oil at the proper temperature for efficient distillation. Another interesting use of electrical measuring instruments is found in the control of chemical processes by the electrolytic conductivity method. Considerable has been done along this line during the last few years.

Experience has shown that, in many instances, actual control of process by automatic means is inadvisable. Frequently there are so many variables involved that control by means entirely automatic would require costly and complicated apparatus. A type of process control that has been found very satisfactory under such conditions is known as the "signal-light system." According to this system, signal lights of various colors are lighted when the various stages of the process are reached. The operator then uses the signals as an indication of the operations necessary and manually puts into action the proper control. Signal-light control possesses the advantages of simplicity and low maintenance cost.

An interesting illustration of this type of control is involved in the electrolytic conductivity equipment used on some of our battleships for salinity control of fresh water and boiler feed. A conductivity cell is placed in the distillate line from the evaporator. The resistance of this cell is measured by a Wheatstone bridge, signal-light controller, which automatically lights the signal lamps according to the conductivity of the distilled water. The calibration of the apparatus is such that a white light is lighted if the concentration is under 0.5 of a grain of chlorine per gal. At over 0.5 of a grain and under 5 grains' concentration a green light is lighted. If the concentration becomes excessive and above 5 grains per gal., a red light is lighted. The signal lamps are placed in the evaporator room so that the operation of evaporators and the disposal of the distilled water may be controlled according to their indications. In event of a red lamp being lighted the distillate is diverted into the

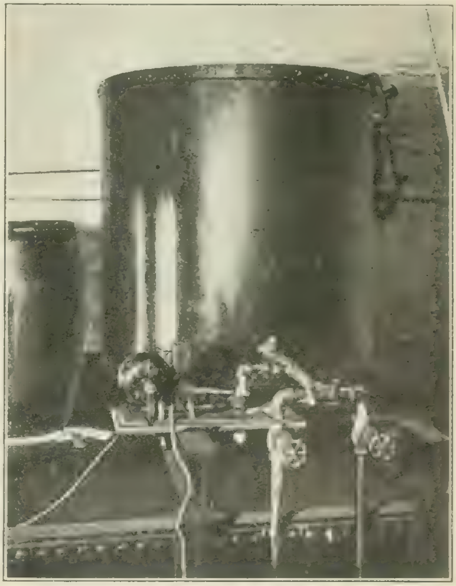

Fig. 3

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[1] "A Meter for Measuring Alkalinity of Boiler Feed Water," *Power*, May 16, 1922.

[2] This Journal, 14 (1922), 395.

bilge as being unfit for boiler feed and other requirements. The condensed steam lines from the main turbine condensers are similarly equipped with signal-light controllers to indicate leakage of the circulating water into the condensate.

A new instrument for recording turbidity of solutions has been recently developed that may have considerable application in automatic process control. Fig. 4 shows the apparatus used in making a turbidity measurement. The solution is interposed between a high candle-power lamp and a photoelectric cell. A 220-volt, d. c. circuit is connected to the photoelectric cell, and a recording potentiometer and shunt used to measure the current flow through the cell. Variations in the intensity of the light falling on the sensitized plate of the cell will vary the number of the electrons emitted and alter the current flow through the cell. It can be seen, therefore, that variations in turbidity of the liquid interposed between the light and the photoelectric cell will result in variations of light transmitted through the liquid, and produce changes of current in the cell circuit. The recording instrument can then be made to effect any suitable control to vary the turbidity and, if desired, maintain it at a constant value.

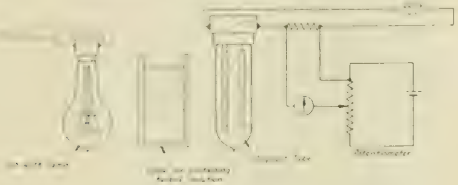

FIG. 4

Control Devices Employed in Testing Ammonia Catalysts[1]

By Alfred T. Larson and Sebastian Karrer

Fixed Nitrogen Research Laboratory, Department of Agriculture, Washington, D. C.

IN THE testing of ammonia catalysts, close regulation of temperature and pressure is essential if the results are to have any comparative value. As a general rule, catalysts do not respond quickly to changes in temperature and pressure, and therefore observations made while either or both factors are fluctuating are not reliable. It will be the purpose of this paper to describe a method of controlling one of these factors—namely, the pressure.

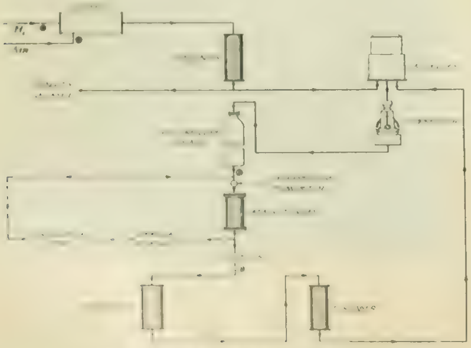

FIG. 1—FLOW SHEET OF CATALYST PLANT

The high-pressure equipment employed in this laboratory for the testing of ammonia catalysts is shown diagrammatically in Fig. 1. It consists essentially of a gas mixer or burner, a gas holder, a compressor, a high-pressure storage, a gas-purifying train (not shown in figure), an electrically heated catalyst bomb, a low-pressure flowmeter, and an ammonia scrubber or decomposer. This circuit requires close regulation of pressure at three places, the first being at the gas burner where hydrogen and air are mixed in such proportions that the residual gas contains three parts of hydrogen and one part of nitrogen. The burner, together with its control apparatus, will be described in the second article of this series.

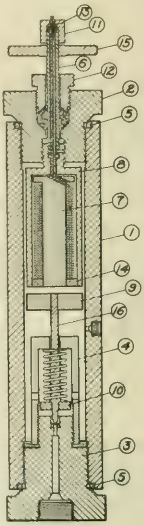

FIG. 2

The catalyst bomb and purification system operateat 1495 lbs. (100-atm.) pressure, while the high-pressure storage may vary from 1600 to 3000 lbs. Between the storage cylinders and the purification towers, therefore, there must be provided a regulatory device capable of delivering gas at a constant pressure (1495 lbs.), while the storage or supply pressure varies between the limits mentioned.

To meet the requirements of high-pressure gas regulation, a type of valve differing somewhat from the common commercial valves has been devised, the details of which are shown in Fig. 2. It consists essentially of a valve seat cut in a steel plug (3), a valve stem (16) held in place by means of a coiled spring, and an electromagnet to lift the valve stem from its seat. Attached to the delivery pipe of the valve is a pressure gage which has an electric contact attached to its Bourdon tube, as shown in Fig. 3. The opening and closing of this contact operates a suitable relay, which in turn opens and closes the electric circuit that energizes the electromagnet. The closeness with which the gas pressure can be regulated is, of course, determined in large part by the sensitivity of the gage.

The valve as designed and built for delivering the gas at 100-atm. pressure has essentially the following dimensions: The supporting shell (1) is a piece of extra heavy tubing

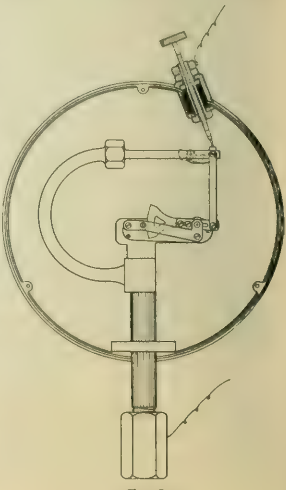

FIG. 3

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[1] Published by permission of the Department of Agriculture.

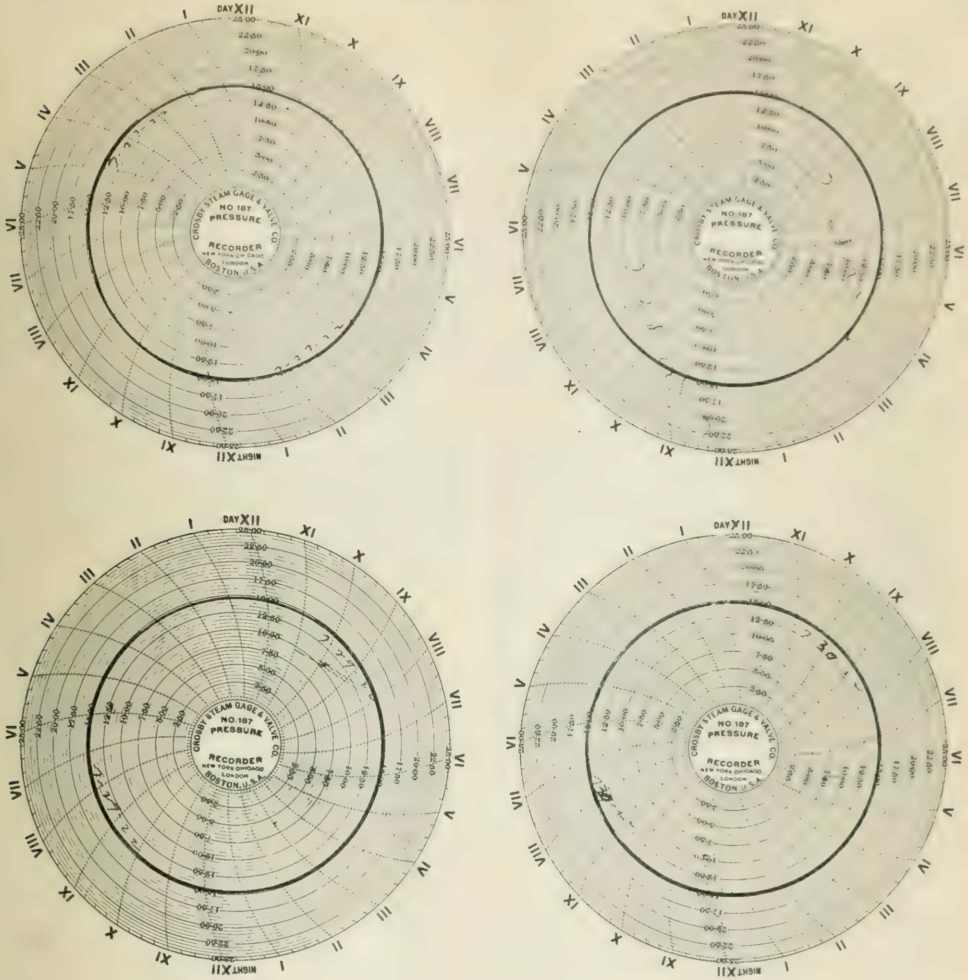

Fig. 4

(length, $11^{1}/_{2}$ in.; o. d., $2^{7}/_{8}$ in.; i. d., $1^{1}/_{7}$ in.), threaded at both ends as indicated in the figure. Into the lower end is fitted a steel plug which serves as a gas inlet and as a valve seat, and also carries the support and guide for the valve stem (16). A $^{3}/_{16}$-in. hole is drilled up to the constriction indicated in the drawing, at which point the hole is reduced to $^{1}/_{32}$ in. A $^{1}/_{4}$-in. drill is run in from the top, leaving the constricted portion approximately $^{1}/_{4}$ in. in length. Into this $^{1}/_{4}$-in. opening is inserted a plug of copper which approximately half fills this hole. The $^{1}/_{4}$-in. drill is now dropped into the hole to smooth the top surface and the $^{1}/_{32}$-in. drill is run through from the bottom. With the valve stem (16) and its support (4) in place, the point of the valve stem is inserted into the copper plug and a seat produced by tapping with a hammer. It was found that a steel valve seat is extremely difficult to make and to maintain gastight, whereas a copper seat requires no grinding and is easily repaired if excessive leakage develops. Most ordinary leaks can be remedied by disassembling the valve and striking the top of the valve stem in a manner similar to that employed at the time when the seat was initially made.

The valve stem (16) was made from a hammered steel rod $4^{1}/_{8}$ in. in length and $^{5}/_{16}$ in. at its greatest diameter. Threaded to the lower portion is a 1-in. iron disk having a thickness of $^{1}/_{4}$ in. and serving as a support for the coiled spring. To the top of the valve stem is threaded a soft iron disk (9), $1^{3}/_{4}$ in. in diameter and $^{1}/_{2}$ in. in thickness. The support for the valve stem (4) is made of brass and is threaded to fit the upper end of 3. This brass shell not only serves as a support for the upper end of the valve stem, but also makes possible the adjustment of the spring which holds the valve stem in place. Four $^{3}/_{16}$-in. holes are cut in the side through which the gas escapes into the outer shell.

The electromagnet (7), which is attached to the upper plug as indicated, is made from a piece of soft iron and is $3^{3}/_{4}$ in. in length and $1^{3}/_{4}$ in. in diameter, and has a wall thickness of $^{3}/_{16}$ in. A brass washer screwed into the bottom of this soft iron shell is drilled and tapped with a $^{3}/_{4}$-in. hole into which is fitted a soft iron spindle (7). This spindle is wound with No. 24 copper wire, one end of the wire being attached to the spindle while the other end passes out through the stem (6). Rod (6) is drilled with a $^{5}/_{32}$-in. hole, through which the insulated lead from the electromagnet passes. The upper end of this wire is passed through a soapstone cone, squeezed into the upper end of rod (6) by means of a compression nut and washer (11 and 13). Rod (6) is fastened securely to the electromagnet, and, by means of a handle attached to its upper portion, the electromagnet can be screwed up or down. The rod is made gastight by means of a stuffing box (12).

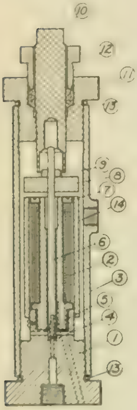

FIG. 5

Since the valve is expected to deliver gas at 1495 lbs., and since the maximum pressure of the gas storage may reach 3000 lbs., it is evident that the valve spring must be adjusted so that there is practically no leakage on a 1500-lb. differential. The spring is therefore adjusted before the valve is assembled by applying 1500 lbs. pressure and screwing the adjustable guide (4) down until the valve stem holds. The valve and electromagnet are screwed into the supporting shell as indicated, the assembly being made gastight by means of annealed-copper ring washers (5). For this particular valve it was found that the magnet could be screwed down so close to its armature that satisfactory operation was obtained with 0.5 amp. at 15 volts. The conventional relay connections to the regulating gage are now made and the valve is ready for operation. In Fig. 4 are reproduced recorder charts showing the operation of the valve for four successive days.

A third point requiring close regulation lies between the low-pressure flowmeters and the ammonia decomposers or scrubbers. In order to make the flowmeter readings comparable, it is necessary to maintain a constant back pressure, 50 cm. of mercury being selected as best meeting the needs at this particular point. This low pressure makes possible the use of a mercury manometer for opening and closing the relay circuit which operates the control valve.

In the case of the high-pressure valve described above, it was desirable that the valve remain closed in the event of a failure on the part of the electrical system. For regulating the back pressure on the flowmeters, however, the valve ought to remain open, so that if the control fails to operate no excessive back pressure will develop. Instead of arranging the magnet so that it lifts the valve stem, as in the case of the high-pressure valve just described, a valve was constructed in which the valve stem was pulled down onto its seat by the magnet. Fig. 5 makes the constructional details of this valve sufficiently obvious so that no further description seems necessary.

Although these valves have been designed to meet the special requirements of an ammonia-catalyst testing plant, it is believed that the principle involved can be readily applied in the solution of other problems where close regulation of gas or liquid flow is essential.

The Plastometer as an Instrument for Process Control

By Eugene C. Bingham, Herbert D. Bruce, and Martin O. Wolbach, Jr.

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IN THE control of processes involving the use of amorphous materials, we often desire something more than a chemical analysis. For example, the analysis of rubber, nitrocellulose, or clay leaves much to be desired, and so physical methods are resorted to. But these methods have proved difficult to handle, owing to the lack of definitive character with this class of substances. Amorphous materials lack a true melting temperature, but, nevertheless, in our need of something definite we try to measure the softening temperature of a bitumen. Colloids do not form true saturated solutions, and therefore the attempt to measure the solubility of, say, nitrocellulose in acetone does not appear promising. It was thought that the viscosity might be definite, but that too appears to be indefinite and to depend entirely on the conditions of the experiment. At first this difficulty only seemed to occur at the higher concentrations of the disperse phase, where the material was said to be plastic. Now we find that all colloidal solutions appear to share this difficulty. A paint supposed to be viscous showed a change of 10 per cent in the viscosity when the shearing stress was scarcely trebled.

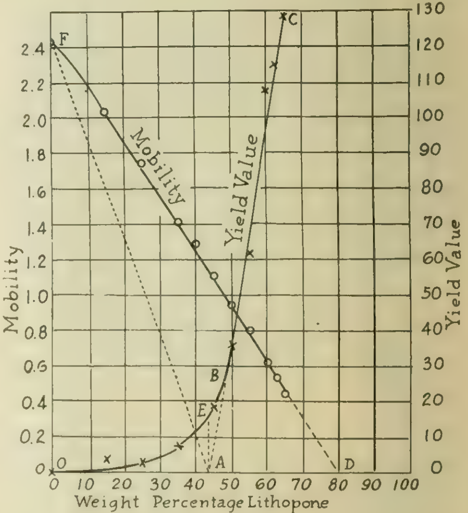


FIG. 1

The variable-pressure viscometer and plastometer promise to do much in removing these difficulties. With a given material a definite shearing stress, known as the *yield value* or *friction*, is required to start the flow. The amount of shearing stress required in excess of this to produce a given flow is a measure of the *mobility*. Since all matter will flow under appropriate conditions, these properties (together with fluidity) are of wide applicability. Moreover, in many cases the flow properties are of direct interest and importance—as in paint, glue, clay, rubber, plastics, etc.

Given a certain paint paste whose yield value and mobility have been measured, if we add varying quantities of vehicle and measure the yield value and mobility, we will obtain curves like those shown in Fig. 1. The mobility increases in a linear manner and reaches the mobility (the fluidity) of the vehicle at zero concentration of pigment. The mobility would have a zero value at a definite concentration, which is probably connected with the relation of the volume of the pore space in the pigment to the concentration of the vehicle. We have, then, a third property which seems capable of exact definition.

The yield value on dilution decreases in a linear manner first, and therefore might be expected to reach a zero value at some finite concentration which we define as the *theoretical concentration of zero yield value.* This is a fourth property, which may be of considerable importance since it depends upon the size of the particle and the adhesion between the particles and the vehicle, but apparently not upon the fluidity of the vehicle.

When the concentration exceeds the theoretical concentration of zero yield value, the material is plastic. However, even when the concentration is very much lower than this so that the particles of the disperse phase do not come within range of each other, the flow is effected and there seems to be always a yield value, although it is no longer a linear function of the concentration, as shown in the figure. We may say that these colloidal solutions are *pseudoplastic.*

We conclude, therefore, that colloidal solutions all exhibit a yield value, whereas true solutions never do. True solutions give us *one* property of fluidity, which suffers an abrupt change at the melting and boiling points. Colloidal solutions give us *several* properties, and these properties differ in a marked manner for the different types of colloids. A simple paint is a colloid of the nonpolar type. The effect of temperature upon it is to increase the mobility in just the ratio that the fluidity of the vehicle is increased, without affecting the yield value.

Quite different is the behavior of a colloid of the polar type, represented by glue and nitrocellulose in acetone. The yield value decreases in a linear manner if the temperature is raised and passes through a zero value, so that we have at this temperature the transition from a plastic material to a viscous liquid, quite analogous to a melting point. We have here a fifth property which appears to be clearly defined. With the plastometer it seems possible to distinguish between the different types of colloids, as well as to distinguish a colloidal solution from a true solution.

The measurements of fluidity of colloidal solutions recorded in the literature must all be regarded as *apparent fluidities* only, and are therefore subject to a plastic correction. This error should be kept in mind wherever measurements of viscosity are used in the control of colloidal materials.

Fluekiger Medal Award

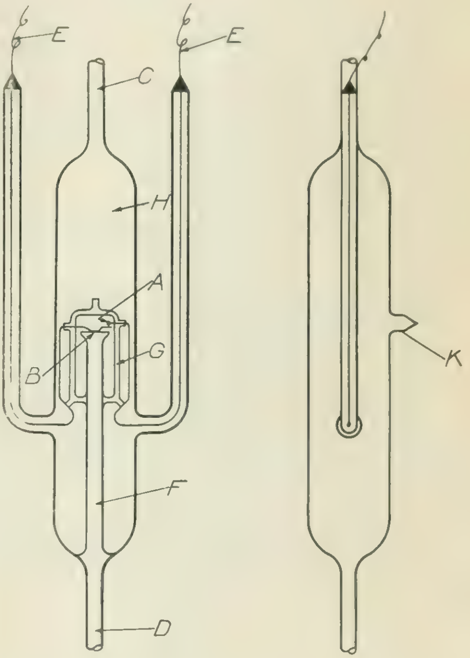
On September 15, 1922, Dr. Frederick B. Power, in charge of the Phytochemical Laboratory of the Bureau of Chemistry, was awarded the Flueckiger Gold Medal by the Swiss Pharmaceutical Society, for his invaluable researches on medicinal plants and essential oils. This medal was established in 1892, in honor of Professor Flueckiger when he retired to private life in Switzerland, after many years of distinguished service as a teacher, writer, and investigator at the University of Strasburg. Without regard to nationality, it is awarded, every five years, alternately by the Swiss and the German Pharmaceutical Societies, for "distinguished services in the promotion of scientific pharmacy." It has hitherto been given to representatives of England, Germany, France, Switzerland, and Austria, this being the first time the honor has been bestowed upon an American. The medal is especially prized by Dr. Power because it bears the name of a most highly esteemed teacher and friend.

Glass Pressure Gage[1]

By S. Karrer, E. H. Johnston, and O. R. Wulf

Fixed Nitrogen Research Laboratory, Department of Agriculture, Washington, D. C.

IT IS often necessary to measure the pressure of a gas or vapor that will react chemically with the materials out of which ordinary pressure gages are constructed. An all-glass gage has been developed for this purpose, and several of them have been in continual use for almost two years. Although a number of glass gages are described in the literature, the present form has proved so satisfactory that it seems worth mentioning.



One form of this gage is shown in the accompanying figure. It consists essentially of a thin glass diaphragm, B, blown on the end of the small tube F, which is sealed into the larger tube H. The diaphragm separates the region D, in which the pressure of the corrosive gas is to be determined, from the region C, containing air whose pressure is measured by a suitable mercury manometer. A change in the gas pressure in either of these regions will cause the diaphragm to deflect. The platinum wire anchored to the glass frame G and resting on the diaphragm at B follows its motion, and will touch a second platinum wire, also fastened to this frame, when the diaphragm moves upward far enough. This contact at A between the platinum wires opens or closes an electrical circuit, including a galvanometer and small electromotive force. Thus, by changing the air pressure on the diaphragm, it may be brought to a definite position, as indicated by the opening or closing of this electrical circuit. The contact A can be adjusted through the tube shown at K in the right-hand figure, so that when the pressure in D is zero a small pressure in C will be required to bring the diaphragm into the position where the circuit is just opened or closed. This pressure must always be subtracted from that necessary to bring the diaphragm back to its zero position, when any actual pressure in D is required.

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[1] Published by permission of the Department of Agriculture.

Tests involving the use of a mercury manometer to connect the regions D and C have shown that the contact can be adjusted to act consistently, and also that the platinum wires remain fixed in position so that the zero point remains constant to within a few tenths of a millimeter of mercury for long periods of time, and under some circumstances the irregularity of the contact is less than can be detected on a mercury manometer. The fact that the contact makes or breaks when the wire is moved through an exceedingly small distance, makes it possible to use diaphragms so stiff that they will withstand several atmospheres pressure difference without breaking.

Daniels and Bright[2] have described a similar gage, but this was found unsatisfactory because the electrical contacts between the platinized surfaces which they used deteriorated very quickly and could not be renewed. In the present form the platinum wire entirely overcomes this difficulty and consequently extends the life of the gage.

In some experiments it was found possible and convenient to use the direct deflection of the diaphragm, as indicated by an optical lever or other device as a measure of the pressure.

Some Phases of Automatic Process Control

By Herbert A. Clark

Taylor Instrument Companies, Rochester, N. Y.

During the initial stages of the development of any process, its control is commonly a matter of close observation on the part of the operator, and of careful hand adjustment to meet conditions as they arise. In many cases frequent changes, sometimes radical ones, are made, as the operator learns what conditions are needed to produce the desired results in the most satisfactory way. As the steps become known, there is a tendency to standardize the process and to make the control automatic as far as it is practicable.

If the desired control is merely to keep temperature constant, some type of thermostat is employed. Many industrial processes of to-day require that the temperature be varied in a predetermined way over a specified length of time. To meet this demand, an instrument has been devised which will automatically vary the temperature of a container at any desired rate, either constant or variable; hold the temperature at any point (between certain limits) for any desired time; remove the condensation in case of steam-heated apparatus; cool the container at any desired rate at the end of the process; stop the process at any desired point, and signal this fact to the operator. This paper will first briefly sketch the fundamental principles on which this device is based, then mention a few possible applications.

The sensitive member of this device (called a "Thermo-Tyme" Regulator) is a so-called *vapor-tension* system (Fig. I), consisting of a metallic bulb partly filled with a liquid, located in the container under control, and a metallic capillary leading from the bulb to an expansion or *capsular* chamber in the regulator case. As the temperature of the bulb varies, the consequent varying vapor pressure of the liquid inside is transmitted through the capillary to the capsular chamber, thus moving one face of the chamber, which in turn operates the control.

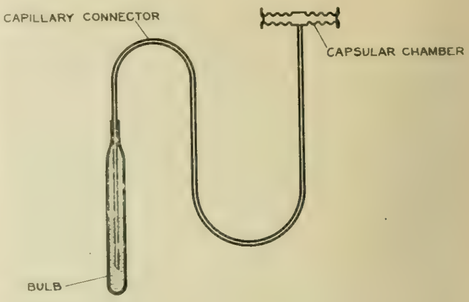

Fig. I—Diagram of Vapor Tension Tube System for Regulator

Fig. II shows diagrammatically the mechanism of the control. Suppose the temperature of a space is to be held above its surroundings—for instance, a steam-heated water bath at 175° F. As the temperature rises during initial heating, the capsular chamber expands until at 175° it has raised the air-valve plunger and opened the valve, thus letting compressed air pass through into a diaphragm which partly closes a valve in the steam line called a ***diaphragm*** valve, thus throttling the steam flow and keeping the temperature constant.

Suppose, on the other hand, that a space is to be maintained at a low temperature—a refrigerator to be controlled at 38° F. by means of cold water circulation. The same arrangement is used but with another type of air valve, one which differs essentially from the one mentioned above only in that the air passage is closed by expansion of the capsular chamber instead of being opened. As the circulating water lowers the temperature of the refrigerator, the capsular chamber becomes deflated. This opens the air valve (called a *reverse action* valve as distinguished from the *direct action*, mentioned above) and the compressed air then partly closes a diaphragm valve in the cold water line, just enough to control the temperature. When using either of the air valves as indicated above, the control temperature is adjusted by hand by turning the eccentric (Fig. II). This obviously varies the distance from the plunger on the air valve to the face of the capsular chamber, thus varying the temperature at which the air valve will open.

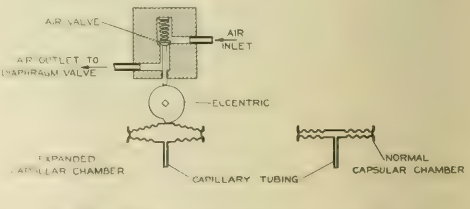

Fig. II—Diagram of Capsular Chamber and Air Valve

So far, we have a mere temperature control. The added time control is accomplished by means of a cam rotated by a clock mechanism, which has the effect of turning this eccentric as desired, although actually it moves the air-valve block up or down instead, thus varying the control temperature. Fig. III shows this time control in simplified form.

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[2] *J. Am. Chem. Soc.*, 42 (1[illegible]), 1[illegible]

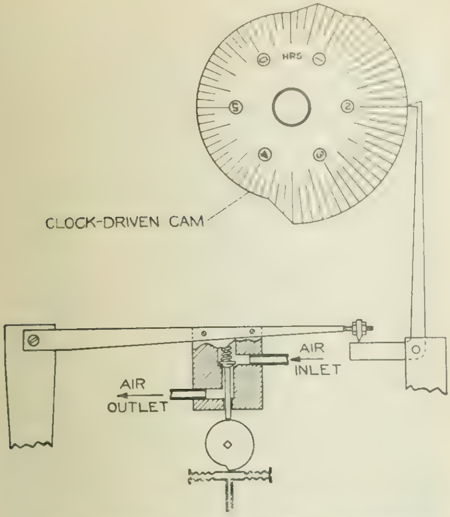

Fig. III—Simplified Diagram of Thermo Tyme Regulator

For instance, with a properly shaped cam, a certain process temperature was raised rapidly from 70° to 100° F., then at a rate a little less than 2° per min. to 170° F. in 45 min., then held constant at this point for 85 min., and finally dropped rapidly to 70° F. again. The rise can be made in successive stages if desired, as shown by the cam in Fig. III and by the temperature record in Fig. IV, although this particular cam does not correspond to this particular chart. Fig. IV is a copy of the record of a process control in which there was a rapid initial rise in temperature to 221° F., 10-min. hold at this point, rise to 247° F. in 5 min., hold at this point for 5 min., rise to 286° F. in 10 min., hold at this point for 1 hr. and 50 min., then a rapid drop to 160° F. in not more than 3 min. The temperature drop can be controlled in the same way.

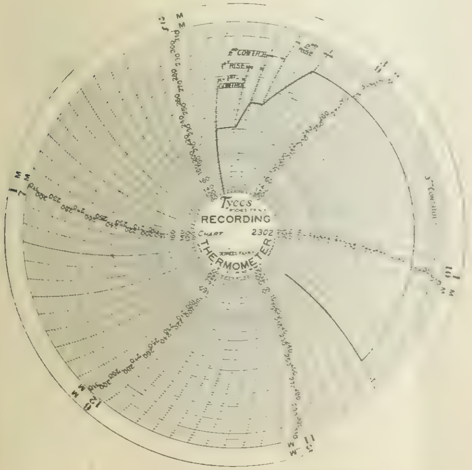

Fig. IV—Record of Process Control

As developed at present, the Thermo-Tyme Regulator will operate between the limits +10° and +470° F., over a temperature range of from 60° to 150° F. for any one tube system, varying with the tube system used.

Fig. V shows the regulator complete with cover open. It will be noted that it has two cams instead of one, each with its own levers, valve, and tube system, one lever and cam being directly behind the other, and consequently partly hidden. One cam may control the temperature of the container, as indicated in Fig. V; and the other, the discharge of condensed steam (if the container is steam heated). In addition, there is a third air valve operated by a trip (not shown) on the cam shaft, to completely shut off the heat supply and cool the container rapidly (by cold water spray if desired) at any predetermined time.

We have indicated in a general way some of the possibilities of this device. Having two cams, each with its own air valve and tube system, independent of each other except for a common cam axis and speed of rotation, and a third valve actuated by a trip when desired, gives great flexibility of adaptation as well as of control. Various attachments which make for convenience and accuracy of adjustment need not be discussed here.

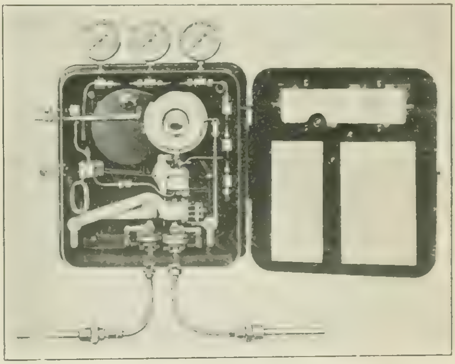

Fig. V—Regulator Complete, Cover Open

Applications

The rubber industry is one in which the process is fairly well standardized. As is well known, however, the exact details of the process vary somewhat with the raw rubber used, with the article being made, and with the judgment of the chemist who has specified the process. The Thermo-Tyme Regulator is adapted to this control as far as the process is standardized, and is now in use in vulcanizing rubber boots and shoes, also automobile tires, especially the larger sizes, to give a uniform cure throughout the mass. One cam controls the temperature-time relations of the vulcanizer, the other adjusts the temperature at which the condensation is discharged. This device is also used in controlling milk sterilizers in the manufacture of evaporated milk.

Another important application is in the dye industry to control dye kettles, thus avoiding the effects of fluctuation in steam-line pressure, reducing the amount of steam used and the amount of vapor in the room, and eliminating streaks and variations of shade in the completed product.

In the drying of magnesia for pipe covering, the initial heating must be done slowly to avoid an excessive drain on the heating boilers, and the final cooling must also be slow to avoid disruption of the dried mass.

To obtain good results in drying macaroni, the temperature should change very slowly (from $^{1}/_{4}$° to $^{1}/_{2}$° F. at a time, in the temperature interval between 90° and 105° F., over a period of from 36 to 48 hrs.).

In the drying of materials such as terra cotta, the Thermo-Tyme Regulator is being used to advantage. In such installations, one bulb is used to control the temperature and the other to control the humidity.

There are many other industrial processes in which the temperature-time relation is significant, and consequently *a priori* considerations indicate in them the usefulness of this device. Some of these may be mentioned—such as nitration and amidizing processes, vacuum drying and crystallizing out of certain chemicals, drying glues, cheese and chip soap, the manufacture of hyposulfites such as Rongalite C. and Hydro N. F., autoclaving, and the manufacture of dyes and intermediates.

Electrical Precipitation in the Chemical Industry

By **P. E. Landolt**

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Much has been written on the application of the Cottrell electrical precipitation processes to various smoke, dust, and fume problems, as well as to specific chemical operations. A review of the subject with particular reference to the chemical industry seems timely.* The unique feature of this method is the use of a high potential electric discharge for the separation of suspended matter, whether solid or liquid, from gases. Owing to the ready adaptation of precipitation equipment by proper design, the Cottrell processes have a wide range of application. They have been applied to high temperature conditions, to conditions of excessive corrosion, and to the economical treatment of large volumes of gases.

Many applications of these processes (in fact, the original investigations of Sir Oliver Lodge and Dr. F. G. Cottrell) have been made to abate a nuisance, but frequently the net return on these installations has been very large. Valuable materials have been saved from waste gases by this means, the processes thus serving not only the community directly but industry itself. The developments along these lines indicated further possibilities, later making these processes an integral part of many industrial operations.

Sulfuric Acid Manufacture

The applications of the Cottrell processes to sulfuric acid manufacture have often been discussed in the literature. The widest application of these processes has been made to the recovery of sulfuric acid mist from (1) exit gases of concentrating apparatus, and (2) exit gases of apparatus such as parting kettles, etc. In these installations, over 99 per cent of the suspended sulfuric acid is continuously removed from the exit gases passed through them. These installations have been made primarily to abate a fume nuisance, but by their operation a great saving in acid has been effected. The net return on their investment in terms of acid removed, deducting fixed charges as well as repairs and all operating charges, has been over 20 per cent.

Owing to the corrosive nature of these fumes, a specially designed precipitator is required. It consists of an all-steel structure on which two lead chambers are hung, one above the other, connected by vertical lead pipes. The discharge electrodes are lead-covered iron wires. A precipitator of this design has a capacity for treating 250,000 to 300,000 cu. ft. of gases per hour with thirty 8-in. pipes 12 ft. long. This type of precipitator has been operated at temperatures ranging from atmospheric up to 350° F., measured at the inlet of the precipitator. Concentration of the acid recovered has varied from 5° Bé. to 60° Bé. The amount of acid recovered has been from 10 lbs. to 300 lbs. of condensate per hour per 100,000 cu. ft. of gas treated per hour. Electric power consumption has averaged 1.0 to 1.5 kw. hr. per 100,000 cu. ft. of gas per hour. The operating voltage has averaged approximately 60,000 volts. The operating cost, including all fixed charges, of these precipitation installations varies from 20 to 25 cents per rated ton concentrated, calculated to 66° Bé.

These processes have been applied to various forms of cascade and tower type concentrators for fresh acid. Within the past year they have been applied successfully to sludge acid concentrators of the "hot air submergence" type, described by Gilchrist.[1]

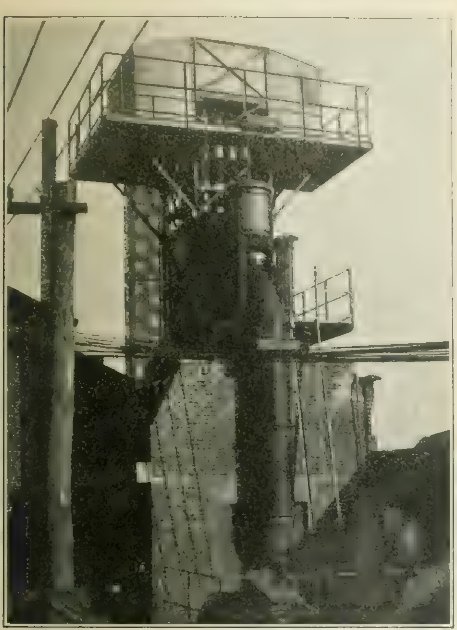
In chamber acid manufacture these processes have been applied to the removal of dust from hot pyrites burner gases. These installations are designed to treat such gases at 1000° F. The precipitator is built of steel and cast iron with a firebrick and sil-o-cel lining to minimize heat loss. Ninety-nine per cent of the suspended dust is removed continuously. Operating cost, including all fixed charges, of these installations has been found to be approximately 20 cents per ton of chamber acid produced. Within the past year the development of new designs of equipment indicates a substantial reduction in these costs. The wide use of elemental sulfur for sulfuric acid manufacture has greatly reduced the need of this type of installation. Its application is now limited to specific locations where pyrites can compete with sulfur. The application of this apparatus to zinc ore roasting was begun about eight years ago, but has not been completed. In Germany, however, an installation of this character has been perfected and is in operation. It is expected that this application in the United States will be completed just as soon as conditions warrant. The plant where this development was started is not roasting zinc concentrates at this time.

Welsh, Schmidt, and Bradley have shown the possibilities of these processes if directly applied to chamber acid plant

* Selected bibliography at the end of the article

[1] *Trans. Am. Inst. Chem. Eng.*, June **1922**.

operation. They would use the action obtained in the electrical precipitator to promote the reaction between sulfur dioxide, oxygen, and water to form sulfuric acid and to remove the acid formed from the field of reaction. The value of this application would be in the reduction of chamber space, reaction control, and over-all size and cost of plant.



Cottrell Precipitator for Sulfuric Acid Recovery

In contact acid manufacture the use of the Cottrell processes for dust removal is the same as that described for chamber acid manufacture. For the purification of the sulfur dioxide gases after cooling, another important application has been found and demonstrated. Actual tests of such installations have shown that over 99.5 per cent of the suspended sulfuric acid mist with other impurities, such as arsenic, have been removed continuously, reducing the renewal of filters, asbestos or mineral wool, from 20 or 30 to 1. Saving has been effected in the materials used, acid saved, and notably in the reduction of power required to overcome the resistance of the filters, particularly when they become clogged. Increased activity of the platinum mass as a result of more perfect purification has also been shown.

Exit gases from the absorbers have also been treated, and under conditions where such gases are conditioned, so that all of the sulfur trioxide is in the form of sulfuric acid mist, complete recovery can be made.

Hydrochloric Acid

Hydrochloric acid has been precipitated from gases from pickling operations, and from chloridizing roast operations. Acid up to 12 to 14 per cent concentrations has been recovered. Nitric acid up to 40 per cent concentration has been recovered in large quantities from nitrating operations. In the case of hydrochloric acid, the difficulty of the problem lay in the selection of suitable materials for the precipitation of the acid—*i. e.*, the discharge and collecting electrodes. The discharge electrodes are made of an alloy resistant to dilute hydrochloric acid and the collecting electrodes of chemical stoneware, tile or acid-proof masonry. For nitric acid the collecting electrodes are either chemical stoneware or tile pipes, and the discharge electrodes are either aluminium rods or nichrome wire.

Phosphorus Pentoxide

Much attention has been given to the volatilization of phosphorus pentoxide from the reduction of phosphate rock in electric or other furnaces. The volatilized phosphorus pentoxide is removed as phosphoric acid in Cottrell precipitators. This "furnace-condensation-precipitation" method produces a concentrated phosphoric acid, which may be used after purification for various chemical purposes, and with which additional phosphate rock may be acidulated to form a concentrated acid or superphosphate. The use of sulfuric acid is thereby avoided. This phosphoric acid may also be used to fix ammonia, or in combination with potash salts to form a concentrated fertilizer. Commercial plants are in operation. For reference, the publications of Carothers, Waggaman, and others may be consulted.

For the purpose of this paper, no detailed discussion of the applications to metallurgical operation will be given. Reference may be made to the appended bibliography for the literature covering these applications. An important recent development in the metallurgical field is the volatilization-concentration of metallic constituents from complex ores using the Cottrell processes. This work has been carried on by the Western Precipitation Company and Western Metallurgical Co., together with the Bureau of Mines Experiment Station at Salt Lake City, Utah. Arsenic has been recovered as a crude arsenic trioxide by the Cottrell processes. The roasting of Cottrell flue dust effects a concentration of the arsenic. By temperature control and reprecipitation, a crude arsenic trioxide of over 90 per cent content is obtained. This crude arsenic is refined in a "kitchen" and a precipitator is again used on the exit of the "kitchen."

Other Applications of Cottrell Processes

The industrial gas field is a chemical industry, and brief reference is given here to certain applications in this field which have a bearing on chemical operations. The detarring of by-product gas and illuminating gas by the Cottrell processes permits the recovery of a dry tar by temperature control, together with the direct recovery of ammonia, and the production of a high-grade ammonium sulfate.

The dry, hot cleaning of iron blast furnace gases has been demonstrated commercially and installations for this purpose are in successful operation. Where iron ores and fluxes carry appreciable potash, the dust and fume recovered by the precipitator contain a high percentage of water-soluble potassium oxide. Dust recovered has analyzed from 6 to 8 per cent to over 20 per cent water-soluble potassium oxide. This is a potential source of by-product potash. Other sources of potash recovery have been shown, such as portland cement kiln dust and fume recovery, and fume recovery from molasses slop incineration. Cement plants equipped with Cottrell precipitators have been operated during the recent war for the potash recovered with cement as a by-product. In fact, raw materials containing appreciable potash were added to the charge to increase the potash fume recovery.

Wood distillation offers an attractive field for electric precipitation. Hawley and Pier[2] showed experimentally the possibilities of electrically detarring gases from hardwood distillation. Calculated steam saving on subsequent distillation of the acetic acid and methanol in a 100-cord plant has been shown to be at least $25 to $50 per day, based on a steam cost of 75 cents per ton.

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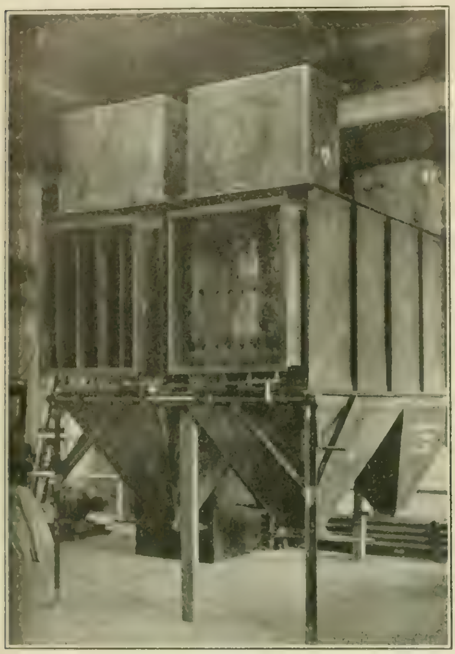
[2] *Chem. Met. Eng.*, **26** (1922), 1031.



COTTRELL PRECIPITATOR FOR USE WITH SPRAY DRYING EQUIPMENT

In the preparation of soda and sulfate pulp, the Cottrell processes have been used for the recovery of soda salts from the incineration of the waste liquors. A plant installed for this purpose has proved a good return on its investment.

In order to produce finely divided solid products for various purposes, spray evaporation processes have been developed in which fuel, labor, and power savings have been obtained together with certain physical properties of the finished products. The Cottrell processes are being applied to collect such finely divided particles. Here the case of adapting the apparatus to a great variety of conditions, together with the saving in power, uniform pressure on the dryer, as well as other considerations, make these processes highly desirable.

In a paper limited to a review of the subject, it is impossible to outline all of the possible applications or to give full details of operation, equipment, and cost on any one application. It is desired, however, to put before those interested in chemical plant operations the fact that the Cottrell processes are a means of great help to the chemical plant in the treatment of gases, for purification, fractional condensation, concentration or other purposes.

BIBLIOGRAPHY

1—M. Hohlfeld, "Das Niederschlagen des Rauchs durch Electricitaet," [illegible] 2 (1824), [illegible]

2—C. F. Guitard, "Condensation by Electricity," *Mechanic Magazine*, **53** (1850), 346.

3—[illegible] "The [illegible] Deposition of Dust, Smoke, etc.," *J. Soc. Chem. Ind.*, **5** [illegible]

4—F. G. Cottrell, "The Electrical Precipitation of Suspended Particles," *J. Ind. Eng. Chem.*, **3** [illegible]

5—W. A. Schmidt, "The Control of Dust in the Portland Cement Industry," *Proc. 8th Internat. Congr. Appl. Chem.*, **5** (1912), 117.

6—A. H. White, "The Electrical Separation of Tar from Coal Ash," *Am. Gaslight J.*, **97** (1912), 210.

7—W. H. Howard, "Fume Precipitation at Garfield," *Am. Inst. Min. Eng.*, **49** (1914), 540.

8—F. G. Cottrell, "Problems in Smoke, Fume and Dust Abatement," *Smithsonian Institution Report for 1913*, Pub. No. 1307, **1914**, 653.

9—W. W. Strong, "Theory of Electric Precipitation," *Proc. Am. Inst. Elec. Eng.*, **34** (1915), 220. A. F. Nesbit, "Theoretical Experimental Considerations of Electrical Precipitation," *Ibid.*, **34** (1915), 507. L. Bradley, "Practical Application of Electrical Precipitation," *Ibid.*, **34** (1915), 523.

10—W. A. Schmidt, "Cottrell Processes of Electrical Precipitation," *Trans. Can. Min. Inst.*, **18** (1915), 110. C. H. Aldrich, "Treatment of Silver Furnace Fume by the Cottrell Process," *Trans. Am. Electrochem. Soc.*, **28** (1915), 119.

11—L. D. Ricketts, "Dust Losses in Copper Smelting," *Eng. Min. J.*, **102** (1916), 396.

12—A. F. Meston, "Electrical Precipitation in the Chemical Industries," *Electric J.*, June **1917**, 248.

13—J. N. Carothers, "Electric Furnace Smelting of Phosphate Rock and Use of Cottrell Precipitator in Collecting Volatilized Phosphoric Acid," *J. Ind. Eng. Chem.*, **10** (1918), 35.

14—A. A. Heimrod and H. D. Egbert, "The Cottrell Processes in the Sulfuric Acid Industry," *Chem. Met. Eng.*, **19** (1918), 309.

15—H. D. Egbert, "Cottrell Process and Its Application to Foundry Dust Problems," *Trans. Am. Foundrymen's Assoc.*, **27** (1918), 266.

16—J. G. Davidson, "Electrical Precipitation of Tar Fog," *Trans. Can. Min. Inst.*, **21** (1918), 252.

17—E. E. Thum, "Notes on Electrical Precipitators," *Chem. Met. Eng.*, **20** (1919), 59

18—A. B. Lamb, "Portable Electrical Precipitator for Smokes and Bacteria," *Trans. Am. Electrochem. Soc.*, April **1919**.

19—N. H. Gellert, "Electrical Cleaning of Blast-Furnace Gas," *Blast Furnace Steel Plant*, July **1919**.

20—W. C. Smith and A. A. Heimrod, "Application of the Cottrell Process to the Recovery of Fume from Silver Refinery Operations," *Chem. Met. Eng.*, **21** (1919), 360.

21—N. H. Gellert, "First American Potash from a Blast Furnace," *Am. Fertilizer*, September 13 (1919), 64; "Electrical Cleaning of Gases as Applied to Blast Furnace," *J. Phila. Engrs. Club*, December **1919**, **449**.

22—P. E. Landolt and H. M. Pier, "Air Cleaning by the Cottrell Electrical Precipitation Processes," *J. Phila. Engrs. Club* April **1920**.

23—R. C. Tolman and S. Karrer, "Motion of Droplets and Particles in the Field of Corona Discharge," *Chem. Met Eng.*, **22** (1920), 1203.

24—A. Delasalle, "L'Epuration Electrique des Fumées et des Gas dans le Service des Poudres Pendant la Guerre," *Chimie et Industrie*, September **1920**, 291.

25—P. E. Landolt, "Eliminating Waste and Nuisance in Smoke Fume and Gas," *Chem. Met. Eng.*, **25** (1921), 428.

26—W. Kee and F. H. Veits, "Cottrell Electrical Precipitator at American Acid Company," *Chem. Age*, February **1921**, 71.

27—E. Anderson, "Recent Progress in Electrical Precipitation," *Chem. Met. Eng.*, **26** (1922), 155.

28—L. F. Hawley and H. M. Pier, "Application of Electrical Precipitation to the Wood Distillation Process," *Chem. Met. Eng.*, **26** (1922), 1931.

29—A. M. Fairlie, "Cottrell Process in the Sulfuric Acid Industry," *Chem. Met. Eng.*, **25** (1921), 861.

Course in Chemistry for Salesmen

The Salemen's Association of the American Chemical Industry warmly received the suggestion of Dr. F. E. Breithut, of the College of the City of New York, that a special course of lectures on chemistry be inaugurated at the college for the benefit of the chemical salesmen. The official announcement was made at a meeting of the New York chapter of the Association held at the college on October 13. Following the announcement, 33 members of the Association expressed a desire to enroll for the course, which is to consist of ten lectures and to be limited to 50 members of the Association. The course is to begin in January and to be given one evening a week.

The officers of the New York Chapter are:

Chairman: JOHN A. CHEW, Warner Chemical Company
Secretary: D. H. KILLEFFER, *Journal of Industrial and Engineering Chemistry.*
Treasurer: GEORGE ASHWORTH, Dow Chemical Company.

A new society called the "Kolloidchemische Gesellschaft," and devoted to pure and applied colloid chemistry, has recently been formed at Leipzig. At the organization meeting on September 15, eighteen chemists and physicists spoke on the relations of colloid chemistry to other sciences and to industry.

The Ajax-Wyatt Furnace in the Brass Mill Casting Shop[1,2]

By Russell P. Heuer[3]

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The application of the Ajax-Wyatt type furnace to the brass-mill casting shop is shown in this paper. The construction of this type of furnace and its casting equipment is illustrated, and a method of bringing the furnace into better electrical balance is developed. The operating characteristics of the improved furnace are investigated and its performance compared with that of the coal-fired crucible furnace.

IN A PAPER before the American Electrochemical Society on April 23, 1921, Dr. Gillett of the U. S. Bureau of Mines has enumerated as of January 1, 1921, 323 electric furnaces melting brass and bronze in commercial use in this country, and an additional 70 units planned for prompt installation. Of those in use 126 are arc furnaces, 98 vertical ring induction furnaces, 86 reflected heat furnaces, and 13 of miscellaneous other types. There are 16 different makes represented. In the brass rolling mills alone there are 5 different makes in use, with a total of 112 units. Of these 26 are arc furnaces, 85 vertical ring induction furnaces, and 3 reflected heat furnaces. The 70 units projected are for rolling mill use—all of the vertical ring induction type.

CONSTRUCTION OF FURNACE

The vertical-ring induction furnace makes use of the patented Ajax-Wyatt heating element. In principle it is very simple. Electric energy is converted into heat within the metal to be heated by virtue of this metal's resistance to an electric current which passes through it. The furnace is essentially an electrical transformer, which, when properly supplied with electric energy, induces the necessary currents to flow in the metal content of the furnace and produce the heat required. A view of one such unit of 1000-lb. capacity appears in Fig. 1. The outer casing as shown consists of two bronze castings and a steel upper jacket. The refractory lining is carried therein, being separated by heat insulating bricks from all parts of the casing. The lining is usually of the rammed-up type, being formed *in situ* under a pneumatic hammer, using wood forms for shaping the furnace interior. The lining material generally used is a type of refractory clay, bonded with 5 per cent sodium silicate and 5 per cent fiber asbestos. The ramming and drying of such a lining so that it will not develop cracks and leak molten metal when operating require considerable skill and experience. The main metal reservoir or crucible of the furnace can carry up to 1200 lbs. of molten brass. Opening into the bottom of this crucible are the ports of the resistor tubes. These tubes carry the molten metal through which the heating current passes. They form a single-turn secondary, short-circuited on itself and linked by the alternating magnetic flux from a 40-turn primary coil connected to 60-cycle, 220-volt, power supply mains. These resistor tubes are formed in the refractory lining using 3 by $^3/_4$ in. cores, about 41.2 in. of equivalent length for this cross section.

METHOD OF OBTAINING WELL-BALANCED MECHANISM

It is necessary that the tube area and length, the primary voltage and number of turns to the primary coil be properly apportioned to obtain an efficient, well-balanced mechanism. The set-up can be viewed as a transformer in which all power transformed into the secondary appears as Joule heat in this circuit. It is desirable to obtain the maximum power factor for the specific power rating required—usually the maximum power obtainable.

$$\text{Now, } W = E\,I\cos\theta \tag{1}$$

$$= \frac{E^2 R}{X^2 + R^2} \tag{2}$$

where W = primary power
E = primary voltage
I = primary current
$X + R$ = equivalent reactance and resistance of the furnace
θ = phase angle

For any value E, W has a maximum when

$$X = R \text{ or } \cos\theta = {}^1/_2\sqrt{2} \tag{3}$$

$$\text{But}\quad R = r_1 + r_2\frac{N_1^2}{N_2^2} \tag{4}$$

$$r_2 = k\,\rho\,\frac{l}{a} \tag{5}$$

where $r_1 + r_2$ = primary and secondary resistance
$N_1 + N_2$ = primary and secondary turns
k = constant
ρ = specific resistance of metal of secondary
$l + a$ = length + area of secondary circuit

Now, a must be of sufficient size to allow the secondary current density per unit sectional area a safe value below that which will cause "pinching off" of the molten metal. To keep a high, R and therefore X must be held at the minimum.

Gin[4] develops the approximate relation

$$\operatorname{Tan}\theta = \frac{4\pi\omega N_2^2}{r_2}\cdot\left(\frac{1}{R_1} + \frac{1}{R_2}\right) \tag{6}$$

where R_1 = reluctance of magnetic circuit linking the primary but not the secondary; R_2 = reluctance of magnetic circuit linking the secondary but not the primary; and ω = cycles per second.

$$\text{Since }\tan\theta = \frac{X}{R} \tag{7}$$

$$X = \frac{4\pi\omega N_2^2}{r_2}\cdot\left(\frac{1}{R_1} + \frac{1}{R_2}\right)\cdot\left(r_1 + r_2\frac{N_1^2}{N_2^2}\right) \tag{8}$$

$$X = 4\pi\omega N_2^2\cdot\left(\frac{1}{R_1} + \frac{1}{R_2}\right)\cdot\left(\frac{r_1}{r_2} + \frac{N_1^2}{N_2^2}\right) \tag{9}$$

Of the factors determining X, the expression $\left(\frac{1}{R_1} + \frac{1}{R_2}\right)$ represents the concessions necessary in constructing a transformer whose secondary is of high temperature molten metal. Physical conditions impose its minimum value. With the factor $\left(\frac{r_1}{r_2} + \frac{N_1^2}{N_2^2}\right)$ the first term constitutes about 2 per cent of the total value, from which it is evident that in adjusting R to X, r_2 may be varied with but little change in X. The prevailing rolling mill furnace of 40 primary turns yields on test the approximate value $X = 0.40$ ohm.

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[1] Received June 20, 1922.

[2] A thesis submitted in partial fulfilment of requirements for graduate degree of Ch.E.

[3] Formerly in charge of electric furnaces, Chase Metal Works, Waterbury, Conn.

[4] *Trans. Am. Electrochem. Soc.*, **12** (1909), 101.

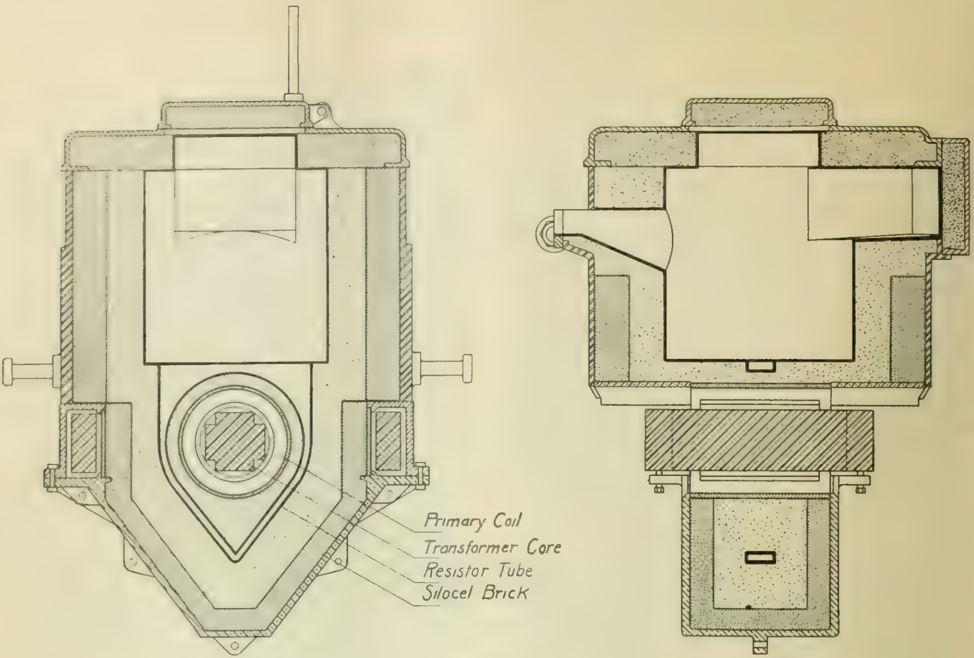

FIG. 1

With this as a value for R, r_2 may be developed for a maximum W. The tube length l has come to its present value, 41.2 in., as a safe-working convenient dimension. Further increase might be favorable but the point needs experimental verification. ρ is naturally determined by the metal of the bath, and k is a constant greater than unity owing to skin-effect, etc. The entire factor $K\rho\frac{l}{a}$ is readily adjusted by grouping $K\rho l$ together, determining this value from operating furnaces and varying a to give the required R.

With X and R fixed, W and E are related as shown in Fig. 2.

To obtain maximum power input, E is increased until the secondary current reaches its maximum safe value before pinching occurs. If E cannot be raised, N_1 is reduced to give the equivalent effect. Variation of N_1 should not affect Θ (Equation 6). Test values of a furnace apportioned as above show:

X = 0.398 ohm
R = 0.405 ohm
W = 71.5 kw
E = 5.95 volts per primary turn
Cos. Θ = 0.715

This furnace operated well on 65 : 35 brass. If the maximum power input is not required, a should be lowered until W, E, and a are adjusted as desired. In operating the same furnace on varying copper mixtures, ρ varies and R changes accordingly. A furnace tested as above gave:

Copper Per cent	R Ohms
[illegible]	0.501
[illegible]	0.493
[illegible]	0.468
75.57	0.450

This variation in R changes Θ and W, and special provision is necessary if widely varying metals are to be melted.

OPERATION

In operating the furnace, the resistor tubes must be filled with molten metal at all times, to establish the continuity of the secondary circuit. In starting a new furnace or restarting an idle one, the tubes are "primed" with a 200-lb. charge of molten metal from some extraneous source. This done, the closing of a switch connecting 220 volts to the primary coil places the furnace in operation. The charge to be melted is fed into the molten button in the bottom of the furnace, using the top and rear charging doors. Copper, spelter, and scrap may be added in any sequence desired. The furnace runs unsealed, but is almost entirely free of zinc-fume while running.

The bath is heated from the bottom, and the bulkier portions of the cold, unmelted charge remain on top of the heat, preventing oxidation or zinc loss. When melting is complete, heating is continued until the pouring temperature is reached. Then the power supply is reduced to 70 volts, and the power input falls to about 8 kw., an amount sufficient to hold the metal indefinitely at its pouring temperature. The surface of the bath is dry-skimmed and pouring is started. Many different pouring methods are used with the induction furnace, one of which is illustrated in Fig. 3.

Here the furnace pours directly into the molds, being tilted on trunnions centered about the furnace spout. Hydraulic cylinders beneath the furnace furnish the tilting power, the rate of tilting being controlled by a hand-operated valve. The necessary molds are mounted on a turntable which permits the bringing of each successive mold rapidly into place below the pouring spout. Pouring proceeds under accurate control and constant temperature. Sufficient metal is left in the furnace at the end of its pour to submerge the resistor tubes and furnish a button for the next heat. Operation continues 24 hrs. daily, and in event of week-end or other shut-downs, it is necessary to apply the 8-kw. input to keep the bath molten. Freezing of the metal content of the furnace usually is fatal to a furnace lining, the attendant shrinkage being enough to crack the refractory and allow molten metal to leak through when operation is resumed. For an extended shut-down an operating furnace should be drained of metal and cooled down slowly to avoid cracking the lining. With usual precautions, operation may be resumed when desired.

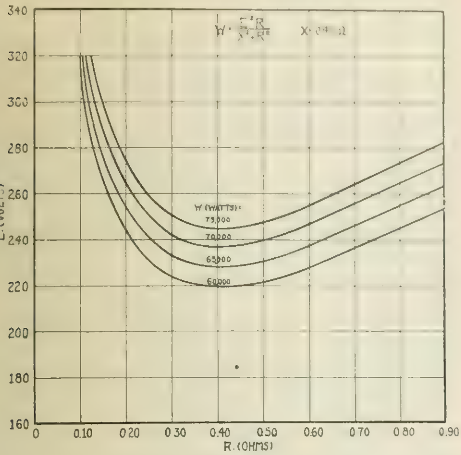

Fig. 2

Practically all castings for rod, wire, sheet, or tube manufacture, excepting those of nickel-silver, bronze, or copper metal, can be made with the furnace. In the latter cases, the furnace is unable to operate, owing to failure of the lining material with the temperatures attained. New refractories are under development, however, with which it is hoped the difficulty will be overcome.

Changing furnace production from one alloy to another requires special procedure to correct for the 200-lb. starting button which the new alloy will pick up from the alloy preceding it. Furnace schedules are usually arranged so that the change is merely one in zinc-copper ratios—a matter of adding a given amount of either spelter or copper to correct the button of old alloy. Occasionally, however, the change requires the elimination of a third metal such as tin or lead, in which case the old button is poured out and a new button poured in from some extraneous source.

The furnace is admirably suited to the large-scale production of the modern brass rolling mill. Furnace installations of 24 units are already operating, and 30- and 40-unit batteries are in course of construction. On this scale, production schedules of diverse alloys, casting sizes, etc., can be filled with minimum changing of individual furnace programs. Operating units are often assigned to constant running, 24 hrs. daily, 6 or 7 days weekly, with neither mold nor metal change.

Comparison with Coal-Fired Crucible Furnace

The expansion of the induction furnace into the rolling mills has been largely at the expense of the crucible process. To compare the two processes is interesting. Considering quality of product, the crucible process at its best can produce metal in no wise inferior to electric furnace brass. But to keep the crucible process at its best is a difficult matter. Consider first the chemical specifications to which the metals must conform. The making of crucible brass involves a loss of more than 3 per cent of the zinc content of the charge. The quantity varies with the kind of charge, the method of melting, the temperature reached before pouring, the time the metal remains at this temperature, etc. Again, with crucibles there is often lost into the fire some of the nonvolatile metals either while charging or later, owing to crucible leaks or spilling. With these high and variable losses, close chemical control is often difficult to obtain. Then, too, the process of adding the spelter to a pot of brass requires proper hand-stirring to distribute the zinc uniformly through the charge. Occasionally the metal cast from the top of the crucible charge is higher in zinc than that cast from the bottom.

We eliminate these human factors of the crucible process with the machine-like action of the electric furnace. The zinc loss is very low, as is seen from Table I, which covers the metal balance of a representative 60-kw. furnace operating on brass of 60 to 70 per cent copper.

Table I

	Pounds	Per cent
Gross charges	3,352,581	100.00
Net castings made	3,285,062	97.99
Net recovery as skimmings and splashings	53,552	1.59
Total metal shrinkage, including oil and nonmetallic in original charges	13,967	0.42

The loss of nonvolatile metals is almost nil. The uniformity of zinc distribution in the furnace charge is insured by the vigorous automatic stirring obtained. The electric current in the resistor tubes gives rise to pinch effect, motor effect, and possibly other forces, which literally squirt a stream of metal from the mouth of each resistor. This action is strong enough to elevate the metal surface over the tubes one inch or more above the level of the metal bath itself. The effect of these low metal losses and the positive mixing are seen in the following analyses. (Tables II, III, and IV.)

Table II—First and Last Pourings from Four Heats of Leaded Metal

Heat No.	First Pourings, Per cent Cu	First Pourings, Per cent Pb	Last Pourings, Per cent Cu	Last Pourings, Per cent Pb
1215	64.44	1.03	64.38	1.05
1221	64.38	1.01	64.38	1.08
1235	64.27	1.09	64.24	1.17
1242	64.49	1.10	64.52	1.02

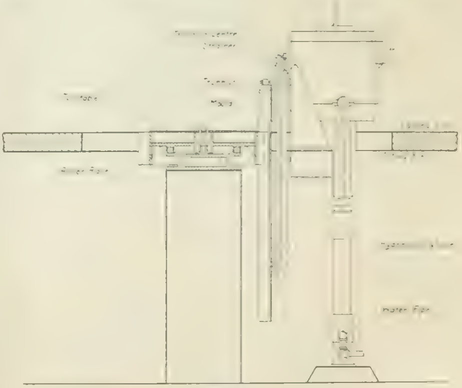

Fig. 3

But of equal importance to chemical analysis are the pouring temperature and conditions attending the casting of the metal. The product must be sound, close grained, free of pipe, blowholes, or included matter, and of smooth surface, no spills, cold-shuts, or other defects. In crucible practice the rate of heating is variable, and the time for pouring is determined only by the operator's judgment. Casting is done under difficult conditions and the *hand* nature of the process makes it require considerable dexterity and physical effort. With the induction furnace the procedure is again machine-like. Heating proceeds at a uniform rate, the furnace meters always indicating the total electric energy put into a given charge at any stage of the melting. The furnace operator knows the average energy requirement for each heat of metal melted (Table V) and by observing the watt-hour meter gets considerable help in determining when to pour.

TABLE III—CONSECUTIVE HEATS OF MUNTZ METAL FOR TUBING

Heat No.	Copper Per cent	Heat No.	Copper Per cent
1	60.78	11	60.22
2	60.56	12	60.21
3	60.50	13	60.36
4	60.55	14	60.38
5	60.48	15	60.56
6	60.34	16	60.43
7	60.50	17	60.83
8	60.58	18	60.70
9	60.07	19	60.38
10	60.40	20	60.50

TABLE IV—RANDOM SAMPLES TAKEN ONE FROM EACH OF 15 SUCCESSIVE 8-HR. SHIFTS

(Production represented—90,000 lbs. rod billets)

Date	Shift	Copper Per cent	Lead Per cent
7-13	I	61.31	2.85
	II	61.27	2.92
	III	61.37	2.85
7-14	I	61.50	2.74
	II	61.53	2.81
	III	61.40	2.73
7-15	I	61.66	2.73
	II	61.50	2.81
	III	61.64	2.88
7-16	I	61.33	2.79
	II	61.63	2.76
	III	61.29	2.83
7-18	I	61.70	2.80
	II	61.44	2.66
	III	61.31	2.71

The furnace ammeter also helps by its so-called "kicking." Kicking occurs when the metal in the tubes is hot enough to form zinc vapor in the secondary circuit. The circuit is temporarily opened and the ammeter oscillates from its normal running position down to zero and then rapidly back to normal as the circuit makes and breaks. The action indicates that the metal of the bath is itself close to the boiling point. As with the attaining of proper temperature, casting conditions with the furnace are very favorable. Hydraulic tilting and rotary mold tables enable close pouring control. The operators are protected from excessive heat, as all external parts of the furnace are cool enough to be touched by the bare hand. In fact, the 9.6 kw. hrs. actually required to pour 2 : 1 brass (Table V), when compared with 8.0 kw. hrs. theoretically required,[5] indicate a thermal efficiency of 83.3 per cent.

TABLE V

METAL	Kw. Hr. to Pour 100 Lbs. (Average Practice)	Probable Pouring Temperature
60 : 40 brass	8.6	1850° F.
65 : 35 brass	9.3	1960° F.
2 : 1 brass	9.6	2000° F.
70 : 30 brass	10.0	2070° F.

Experience with many million pounds of electric metal has proved it to be satisfactory for rod, wire, sheet, and tubing; but a word of warning is not amiss here as there has been considerable electric metal which has come through unsatisfactory. The cause can be laid to overextending the natural advantages of the furnaces—first, in the skill of the labor employed. To be sure, the induction furnace runs very machine-like but unskilled labor cannot complete the process and turn out good castings. Many a perfect heat of molten metal has ended up as scrap castings, owing to poor mold preparation or improper pouring by the operators. Second, in the kind of raw materials used in the furnace charges—the induction furnace has proved capable of reducing to molten state very light scrap, oily borings, and metallic concentrates which the crucible process handles only with difficulty. In some cases, attempts have been made to use 100 per cent of such materials in the furnaces, but the poor initial quality of these charges seems to show up in the finished product as decidedly inferior metal.

In its economic relation to the crucible process, the induction furnace stands preëminent in the rolling mills. One induction furnace and one operator, melting, pouring, and doing all mold work, can in three 8-hr. shifts turn out a daily average of 16,000 lbs. of finished product, the labor cost being 50 per cent of that for coal-fired crucibles. Then, too, the furnace eliminates crucible expense—a factor of some 0.10 cents per pound in rolling-mill work. It also reduces the metal losses to one-third or less of those of the crucible method. Even in refractory costs, which at one time gave some apprehension, the electric furnace may be cheaper than the pit-crucible furnace. One existent induction furnace with an original lining cost of about $200 has melted over 6,000,000 lbs. on its original lining, and still seems good to continue production indefinitely. In fuel charges, the substitution of electric energy for hard-coal fuel is profitable under average conditions. The electric method is not subject to high fuel handling charges or the expense of recovering from coal ashes any metal lost into the melting fire. The induction furnace is probably the most efficient, thermally, of any nonferrous melting equipment. On 24-hr. operations with a Sunday *holdover* at reduced voltage, 60 : 40 brass can be poured at an average total consumption of 180 kw. hrs. per net ton of castings. The character of the electric load is quite satisfactory, graphic wattmeter charts showing a uniform power demand, excepting the few times of "kicking" at the finish of each heat. The load factor is high and the utilization of 37,500 kw. hrs. in a 25-day month with 72 kw. maximum demand is quite possible. The power factor on 60 cycles can be maintained over 70 per cent and with the 60-kw. demand can attain 86 per cent. In maintenance, as well as in interest and depreciation charge, the furnace is more expensive than the pit-fires. The total casting costs naturally vary with different mills, and different cost-keeping and accounting methods, but experience shows that if in round numbers it cost 1.5 cents per lb. to cast metal from pit-fires, the induction furnace can duplicate the production at under 1.0 cent per pound. Assuming crucible melting capacity to be supplanted by electric furnaces in units of 4,000,000 lbs. annual capacity costing installed about $10,000 each, the saving in the first 2,000,000 lbs. melted should pay for each unit. With capacity operation the original outlay would be returned through reduced expenditures twice yearly.

BIBLIOGRAPHY

1—J. B. C. Kershaw, *Engineer*, **131** (1921), 48.
2—E. Northrup, *J. Frank. Inst.*, **190** (1920), 817.
3—G. H. Clamer, *Ibid.*, **190** (1920), 473.
4—G. H. Clamer, *J. Am. Int. Elec. Eng.*, **39** (1920), 1042.
5—O. A. Kenyon, *Iron Age*, **106** (1920), 818, 880
6—R. N. Blakeslee, Jr., *Elec World*, **74** (1919), 642.
7—G. H. Clamer, *Am. Mach.*, **48** (1918), 21.
8—G. H. Clamer, *Metal Ind.*, **17** (1919), 362.

With its issue of September 16, 1922, the *India-Rubber Journal* started the experiment of using a rubber-paper cover, containing one per cent of rubber used as a toughener. It is stated that in this paper the tensile strength and bursting strain are materially increased, while the folding index of the rubber paper is 172 machine-way and 95 cross-way, as against 5 and 6, respectively, for the cover paper previously used by this journal.

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[5] Clamer, *J. Frank. Inst.*, 190 (1920), [illegible].

Gelatin in the Photographic Process[1,2]

By S. E. Sheppard

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The fundamental process in modern photography consists in the making of negatives and positives with gelatino-silver bromide emulsions. The series of operations consists in: (1) making and coating the emulsion, (2) exposure to light, (3) development, (4) fixation, washing; drying, with auxiliary operations such as hardening, reduction and intensification, toning and tinting. For the preparation of the emulsion, the freedom of the gelatin from desensitizing impurities, its relative content of jelling protein and nonjelling hydrolysates, the viscosity of its sols and their setting points, are important. The factors governing the viscosity are discussed in the light of recent work. Exposure is determined by sensitiveness, which again is largely controlled by inhibitory substances in the gelatin. In the subsequent processes, the mechanical strength of the jelly phase, and the swelling capacity of the gel are important, and their measurement and regulation are noted. The importance of the isoelectric point and of the hydrogen-ion concentration for the behavior of the amphotytic gelatin in the photographic process is discussed, particularly in relation to the acid-fixing and hardening bath. The behavior of gelatin jellies on drying is considered to be explicable without recourse to structure theories of the jelly.

Modern photography is almost as much dependent upon gelatin as upon silver salts. The work upon gelatin which is being carried on at the Research Laboratory of the Eastman Kodak Company is naturally chiefly devoted to its use in photography, and the following is an outline of the function and behavior of gelatin in photographic processes.

The two chief classes of photographic material in which gelatin plays a role are: (*a*) gelatino-silver halide emulsion, and (*b*) dichromated gelatin layers.

In the former, the part of the gelatin is fundamentally that of a binder or suspending medium for silver halides, for silver derived from these, or for compounds derived from the silver by reactions subsequent to development of the latent image. In all these cases the special physical and colloid chemistry of gelatin is of great importance for correct understanding of the behavior of the plate or film.

In the second class cited, the gelatin becomes, through the photochemical decomposition of the dichromate, itself art and part of the image.[3] In fact, the whole practice of photographic and photomechanical processes with dichromated gelatin, gelatose, etc., depends upon radical modifications of the properties of these colloids produced by tanning reactions, either directly or indirectly photochemical. This class is of more importance for photomechanical than for strictly photographic procedure, and will not be discussed directly in this paper.

GELATINS FOR EMULSIONS

Although he had forerunners, the credit for preparing the first gelatino-silver bromide emulsion is generally ascribed to Dr. Maddox, of Liverpool, England (1871). His emulsion was prepared by suspending silver bromide with excess silver nitrate in gelatin acidified with nitric acid, and development was effected with acidified pyrogallol to which more silver nitrate was added. Maddox's emulsion, therefore, belonged to the first of the two main classes of sensitive silver halide preparations:

(A) Silver halide formed in presence of excess silver salt includes wet collodion, collodion emulsion, and most printing-out emulsions.

(B) Silver halide formed in presence of excess soluble halide includes both positive and negative emulsions for chemical development.

It was the previous discovery of alkaline development (of collodiobromide emulsions) by Russell which made Maddox's experiment lead the way to the second class of emulsions, which hold first place in importance in modern photography.

The value of gelatin for emulsions depends both upon its physical properties and its chemical composition. It is not necessary to amplify the statement that gelatin is pre-eminently an emulsoid or solvated colloid. The high degree of reversibility of the transition

$$\text{Hydrosol} \rightleftharpoons \text{Hydrogel}$$

at conveniently attainable temperatures is a fact of first importance for its use. The formation of the jelly from the hydrosol is termed *setting*, the converse passage from the jelly to the fluid solution, *melting*, and it has been customary to speak of *setting points* and *melting points*. By the former is understood the temperature at which the solution congealed; by the latter, the temperature at which the jelly liquefied. These temperatures are not coincident, as in the case of a crystal, and corresponding with this thermodynamic indetermination are only empirically definable by experimental conventions. The writer and S. S. Sweet[4] have shown that the *setting-point concentration* curves, or the *melting-point concentration* curves, determined under standard conditions, are more characteristic of a gelatin than single setting or melting points at one concentration, although if these are taken in the region where the "point" varies linearly with the concentration—10 to 20 per cent—a satisfactory practical comparison is usually possible. Technical gelatins are roughly classified as *hard*, *medium*, and *soft*, in terms of the melting point. Using the writer's apparatus, the following typical results were obtained for 10 per cent jellies:

No.	Kind of Gelatin	Setting Point °C.	Melting Point °C.	Trade Description
1	Glue (domestic)	18.2	19.8	Glue
2	Gelatin (domestic)	23.2	25.8	Soft
3	Gelatin (foreign)	22.2	24.8	Soft
4	Gelatin (foreign)	24.8	28.0	Hard
5	Gelatin	25.1	28.5	Hard

In common with other physical properties, the setting and melting points are largely controlled by the hydrogen-ion concentration. With most photographic gelatins this

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[1] Paper read before the New York Section of the American Chemical Society, January 6, 1922, and the Rochester Section, April 17, 1922.

[2] Communication No. 143 from the Research Laboratory of the Eastman Kodak Company.

[3] It may also act as a binder for a pigment, but the pigment is inert.

[4] This Journal, 13 (1921), 423.

corresponds (in 1 per cent solution) to a pH between 5 and 6, under which condition no great variation results. But, as noted later, this important constant should always be determined, in order that due adjustment may be made.

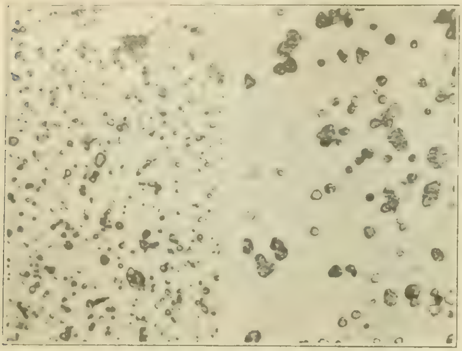

FIG. 1—SILVER BROMIDE GRAINS OF EMULSIONS (MAGNIFICATION 2500)

Apart from this, or in the presence of other ionogens in considerable amount, the value is chiefly determined by the proportion of hydrolyzed to unhydrolyzed gelatin. The value is lower, the more advanced the hydrolysis which converts the protein over into a mixture of proteoses, peptones, and amino-acids.

Recent work of C. R. Smith,[5] R. H. Bogue,[6] and E. T. Oakes[7] has indicated the highly interesting possibility of a thermodynamically definite transition point between "sol" and "gel" forms of gelatin. Smith concluded, from polarimetric measurements of the muta-solution of gelatin solutions, that the point lay between 33° and 35° C., and suggested that it corresponded to a bimolecular condensation of gelatin *molecules*. Bogue, from measurements of the plastic yield of gelatin hydrosols, finds transition at about 35° C., whereas Davis and Oakes,[8] from very valuable studies of the change of viscosity of gelatin solutions with time, have fixed it very precisely at 38.03° C. Some doubt may be felt at present as to the complete validity of these conclusions—that is, as to whether the transition point is independent of the concentration and origin of the gelatin. But the suggestion that what was formerly termed the thermal "lag" of gelatin solution is a case of "suspended transformation" is of great theoretical importance, while the attainment of temperatures of invariance of such a property as viscosity is of equal practical weight.

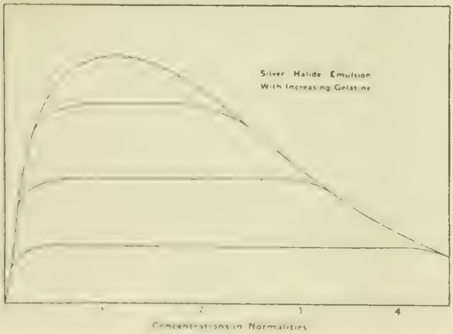

FIG. 2—INFLUENCE OF GELATIN ON AVERAGE GRAIN SIZE OF SILVER BROMIDE

In the preparation of emulsions, including the coating, the properties of the hydrosol are most interesting. They may be divided as follows: (1) protective action, (2) viscosity, and (3) influence on sensitiveness to light.

THE PROTECTIVE ACTION OF GELATIN in the case of gold and silver hydrosols is well known. Values for the *gold number*, by Zsigmondy and others, give:

Gelatin	0.005 to 0.01
Casein	0.01
Egg albumin	0.06 to 0.3
Dextrin	10 to 20

In a recent paper[9] it has been shown that the *gold number* of gelatins depends upon the dilution of the hydrosol, increasing therewith, and upon the age of the solution. It was not found possible to satisfactorily differentiate technical gelatins on the basis of their *gold numbers*.

In the case of silver halide emulsions this protective action, which involves inhibition of agglomeration (and crystal growth) of amicrons, is doubly important. First, we may note that if silver nitrate and potassium bromide solutions, with slight excess of bromide, are mixed in darkness and the precipitated silver bromide washed with water, then it is found to be immediately reducible by any of the usual developers. If quite small amounts of gelatin are added, the reduction is greatly slowed down, and this inhibition increases rapidly with the amount of gelatin, till a maximum effect is soon reached. Sheppard and Mees attributed this protective power largely to the insulation of the silver halide particles from dust, etc., nuclei, with which effect is associated a delay in aggregation of silver amicrons to form larger nuclei. It is possible to prepare colloid-free silver bromide layers, which can give a developable image, but *chemical fog* occurs much earlier.

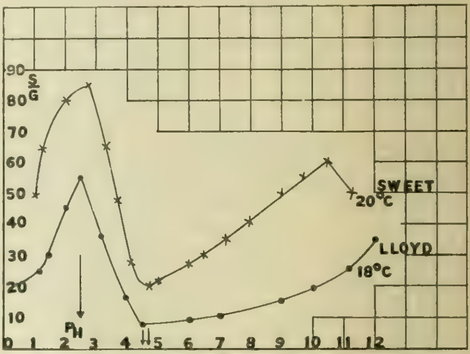

FIG. 3—SWELLING OF GELATIN IN NaOH AND HCl. (S/G = GRAMS WATER PER 1 GRAM GELATIN)

The same protective effect is, however, at work in securing fine-grained precipitates of the silver halide. Emulsions in which the silver halide particles are largely of submicroscopic dimensions are the so-called Lippmann emulsions of silver bromide for interference photochromy, and silver chloride positive emulsions for lantern slides and transparencies. For negative emulsions of higher speed the grain is considerably coarser, being, in fact, definitely crystalline,[10] and one great advantage of gelatin over collodion is that it permits the growth and ripening of the crystals.

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[5] *J. Am. Chem. Soc.*, 41 (1919), 135.

[6] *Ibid.*, 44 [illegible]

[7] *Ibid.*, 44 (1922), [illegible]

[8] Cf. also the valuable studies of Arisz on "The Sol and Gel State of Gelatin Solutions," *Kolloidchem. Beihefte*, 7 (1915), 1.

[9] F. A. Elliott and S. E. Sheppard, THIS JOURNAL, 13 (1921), 699.

Heating suspensions tends to agglomerate the particles and lessen the dispersity, and since negative emulsions are ripened by heat to increase their sensitiveness and density-giving power, it has, therefore, been supposed that high-speed negative emulsions with coarse grains simply represent a stage produced from fine-grained emulsions by heat treatment and Ostwald ripening. This is not the case. The conditions in the preparation of the coarser-grained high-speed emulsions are different, and, in particular, the concentration of the reactants is higher, and that of the gelatin is lower. The importance of these factors is very definitely outlined, if not yet completely covered, by Von Weimarn's theory, and is illustrated in Fig. 2.

The influence of increasing concentration of gelatin in extending the region of minimum dispersity, but lowering the dispersity itself, is illustrated here. Recent work of Odèn[11] indicates that the degree of dispersion of the primary grains of precipitates (gelatin absent) steadily diminishes as the concentration decreases. The maximum observed by Von Weimarn and others is due to secondary aggregation; this may, however, be of equal importance technically.

VISCOSITY FACTORS are as follows:

No.	FACTOR	INFLUENCE	AUTHORITY
(A)	*At one concentration and at one temperature, preferably not below 40° C. and not above 50° C.*		
1	**H-ion activity**	Viscosity is a minimum at pH 4.7 to 4.8, the isoelectric point; rises to a maximum pH 2 to 3.3, and again between pH 8 to 10	J. Loeb R. H. Bogue E. T. Oakes Oakes' conclusions differ somewhat from Loeb's
2	**Cations**—*e. g.*, from ash constituents Na^+ Ca^{++} Al^{+++} Fe^{+++}	Viscosity effect depends upon concomitant pH variation; when pH > 4.8, gelatin combines only with cations. At same pH monovalent cations give same viscosity, polyvalent cations lower than monovalent[12]	J. Loeb
3	**Anions** — *e. g.*, Cl^-	When pH < 4.8, gelatin combines with anions only. At same pH, the monobasic acids HCl, KBr, HNO_3, and acetic acid give identical effect; oxalic, tartaric, succinic, citric, and phosphoric nearly the same as the monobasic acids; H_2SO_4 gives a lower value[13]	J. Loeb
4	**Nonelectrolytes**	Methyl and ethyl alcohol lower viscosity, glycerol and sugars increase. (Compare effect on water)	
5	**Composition and hydrolysis**	Gelatin, even when free from congeners such as mucin, is a mixture of unhydrolyzed and hydrolyzed protein; the greater the proportion of hydrolysates (proteoses, peptones, amino-acids) the lower the viscosity.	Levites von Schroeder R. H. Bogue
6	**Age of solution**	(See Transition)	
7	**Rate of shear**	Inhomogeneous systems—as suspensions, emulsions, colloids—have a lower limit or yield point of shearing stress, below which the displacement is not proportional to the stress. Gelatin sols show *plastic yield*, according to concentration and temperature	E. C. Bingham
(B)	*Concentration variable*		
	Concentration	The viscosity of a gelatin sol increases very rapidly with concentration. The concentration region of interest, photographically, is from 5 to 10 per cent	R. H. Bogue finds that Hatschek's formula is inapplicable *per se*, but may be semi empirically corrected. Davis and Oakes find Arrhenius' formula more satisfactory
(C)	*Temperature and transition*		
1	Temperature	Viscosity decreases with rise of temperature. Furthermore, the rate of hydrolysis increases (depending again upon pH). From recent experiments we find it to be quite perceptible at high and low values of pH, even at 50° C.	S. E. Sheppard and F. A. Elliott
2	Transition	From work on the mutarotation of gelatin sols, C. R. Smith concluded that a transition point between *sol* and *gel* forms of gelatin existed at 34° to 35° C. Bogue measured the viscosity of gelatin sols at different rates of shear, and deduced value from the occurrence of plastic yield.	C. R. Smith R. H. Bogue E. T. Oakes
		Experiments in this laboratory show plastic yield to occur at different temperatures according to the concentration.	S. E. Sheppard and F. A. Elliott
		Davis and Oakes have attacked the problem from the standpoint of time variations of viscosity, and found for their material 38.03° C. a temperature of invariance. Above or below this gelatin-water systems may be in a state of suspended transformation	

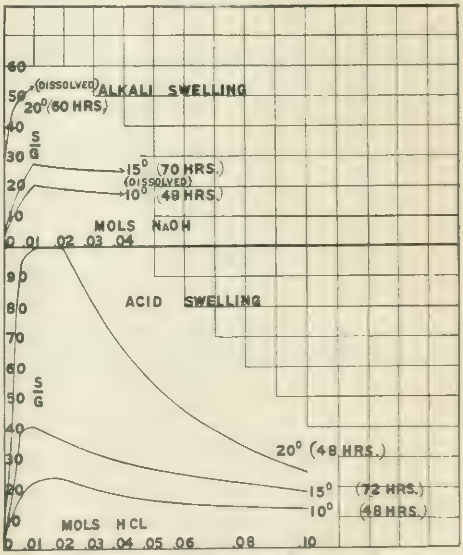

FIG. 4—INFLUENCE OF TEMPERATURE ON SWELLING LIMIT

Photographically, the viscosity of gelatin solutions and of silver halide emulsions is of great importance, since it not only affects the formation of the emulsion, but also controls the operation of coating or spreading.

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[10] Trivelli and Sheppard, "The Silver Bromide Grain of Photographic Emulsions," Monographs on the "Theory of Photography," from the Research Laboratory of the Eastman Kodak Company. Van Nostrand Co., 1921.

[11] *Arkiv Kemi, Mineral Geol.* (*Stockholm*), 7 (1920).

[12] Complications due to precipitation of membranes by trivalent cations excluded.

[13] The other polybasic acids combine with gelatin as monobasic.

The average concentration of gelatin in emulsions is from 6 to 7 per cent, while the sequence of operations in emulsion making, particularly digestion in slightly acid solution at elevated temperatures, may alter part of the gelatin; this is usually only a fraction of the total used. Hence, the viscosity of the given gelatin determines the viscosity of the emulsion, and thereby the coating speed. It is further interesting to note that the coating temperature is usually around 35° to 40° C.—that is, the region of the putative transition point.

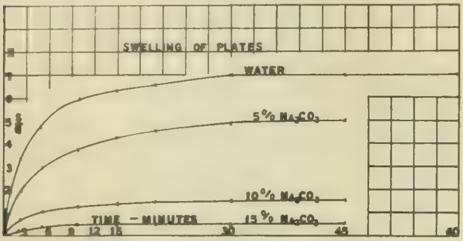

FIG. 5—RATE OF SWELLING OF GELATINO-SILVER BROMIDE EMULSION IN SODIUM CARBONATE SOLUTIONS

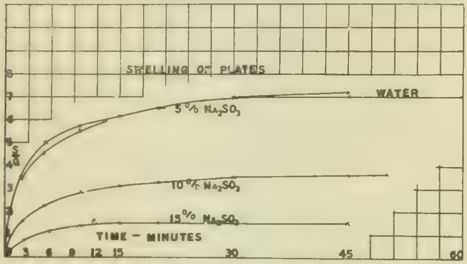

FIG. 6—RATE OF SWELLING OF GELATINO-SILVER BROMIDE EMULSION IN SODIUM SULFITE SOLUTIONS

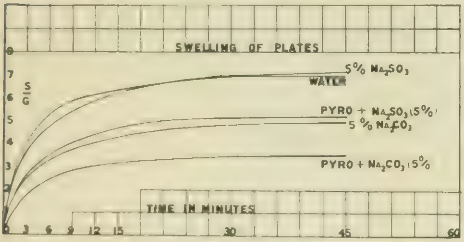

FIG. 7—RATE OF SWELLING OF GELATINO SILVER BROMIDE EMULSION

INFLUENCE ON SENSITIVENESS OF LIGHT—The early conception that the value of gelatin in photographic emulsions consisted in its functioning as a photochemical sensitizer, by absorption of halogen, has been largely abandoned. The most that can be definitely stated at present is that certain impurities must be reduced to a minimum.[14] In regard to the chemical analysis, we may note that the ash should not much exceed 1 per cent, that copper, lead, and iron should be negligible, and chlorides low. On the organic side, organic sulfur, giving silver sulfide, should be absent, also reducing substances (reducing ammoniacal silver nitrate in the dark within 12 hrs.) as well as greasy substances and mucins.[15]

FUNCTIONS OF GELATIN IN NEGATIVE AND POSITIVE MAKING

When we pass from the preparation and exposure to light of gelatino-silver halide emulsions to the operations leading to finished negatives and positives, the properties of the hydrogel are of chief importance. First of these is the *jelly strength*, since, like the *wet strength* of paper, this determines the endurance in many stages of manipulation. Most tests for this, following the time-honored *finger test* for glues, have involved determination of the force required to press a plunger a definite depth into the jelly.[16] These methods are satisfactory for most industrial purposes. There is some possibility of error by *skin formation* at the surface, however, and no definite elastic constant is measured, since both compression and shear are effected in unknown proportions. For these reasons a torsion dynamometer exerting pure shearing stress on jelly cylinders has been designed. This instrument and its operation have already been fully described,[17] so that it will suffice to state that *jelly strength* may be measured therewith, either by the *modulus* of *rigidity*,

$$N = \frac{\text{stress}}{\text{strain}},$$

or by the *torsional resilience* = $^1/_2$ (stress × strain) at limit. Experiments with this have shown that gelatin jellies are rigid and follow Hooke's law nearly up to the breaking point. After molding a jelly and keeping at 0° to 5° C., the rigidity increases rapidly at first, and becomes constant in about 10 to 15 hrs. Between 0° and 10° C. it does not vary much with temperature, but above 10° rapidly falls, to become zero at the *melting point*. The relation of the rigidity to concentration does not follow an identical curve with different commercial gelatins, but it is approximately represented by the equation $N = kc^n$, where n approaches 2, but varies with different gelatins. On varying the hydrogen-ion concentration of ash-free gelatin jellies,[18] for concentrations from 4 to 10 per cent of ash-free gelatin a maximum rigidity (jelly strength) is found at about pH = 8, above which the rigidity falls off rapidly. The decline from the maximum toward lower pH values is less steep, a flat portion, or shoulder, existing near the isoelectric point, but no maximum or minimum. Below pH = 3 there is again a rapid fall. Certain

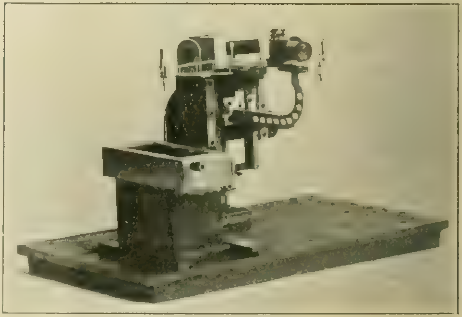

FIG. 8—AUXOMETER

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[14] Cf. B. V. Storr, *Annual Reports of Society of Chemical Industry on Progress of Applied Chemistry*, No. 3, 37 (1918), 405.

[15] Congeners of gelatin, in *chondrin*, and giving slimy precipitates.

[16] A bibliography of these methods is given in a forthcoming monograph by the writer, on "Gelatin and Its Uses in Photography."

[17] THIS JOURNAL, **12** (1920), 1007; *J. Am. Chem. Soc.*, **43** (1921), 539.

[18] Cf. S. E. Sheppard and S. S. Sweet, *J. Am. Chem. Soc.*, **44** (1922), 1857.

anomalies with commercial gelatins have been traced to the influence of inorganic ash constituents; thus aluminium, at 0.01 per cent Al_2O_3 on dry gelatin, greatly alters the curve, a secondary maximum being produced at pH = 4.

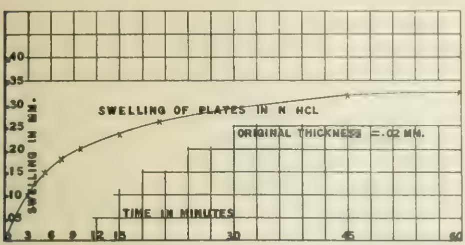

FIG. 9—SWELLING OF GELATINO-SILVER BROMIDE EMULSION IN HYDROCHLORIC ACID

SWELLING OF GELATIN AND PHOTOGRAPHIC OPERATIONS

In the operations of development, fixation, washing, after-operations as reduction, etc., the most important property is the swelling of gelatin in water and aqueous solutions. It is this property which makes the gelatino-bromide *dry* plate or film so amenable to the variety of operations used in photography. Although much current theory is based on the idea that gelatin in swelling does so uniformly in all directions, this is not quite exact. In practice, previous conditions of drying largely determine the subsequent swelling. In the photographic emulsion, the adhesion to a relatively rigid support prevents swelling taking place effectively in any direction but that normal to the surface. Since swelling forces perpendicular thereto do exist, and come into play when the swelling is considerable, the support is substrated with hardened gelatin before being coated with emulsion. It has been known for some time that the swelling of gelatin depends decisively upon the acidity or alkalinity of the solution in contact. This has been developed by H. R. Procter, and H. R. Procter and J. A. Wilson, in terms of Donnan's theory of membrane equilibrium, to explain the swelling quantitatively, at least on the acid side of the isoelectric point. This theory has been discussed very fully elsewhere,[19] and it is not necessary to enter into details. Briefly, it is assumed that gelatin forms a readily ionizable salt with the acid; to secure membrane equilibrium the concentration of diffusible ions in the jelly phase is greater than that of the external solution. The tendency of the diffusible negative ions to diffuse outward is restrained by the cohesion of the jelly, and the increase in volume produced is proportional to the excess concentration of diffusible ion. The agreement of the calculated values with experimental ones is satisfactory; J. Loeb has shown further that if swelling in acids of different concentrations is plotted against the pH of the solution, all effective monobasic acids give nearly identical curves, sulfuric acid, as a dibasic acid, giving somewhat lower values. Swelling on the alkaline side also passes through a maximum at a certain pH. The general form of the swelling curve is illustrated in Fig. 3 and the rapid increase in swelling with rise of temperature is shown in Fig. 4; in this diagram the abscissas are molar concentrations of acid and alkali instead of pH.

In considering the relation of such curves to the photographic process, it must be remembered that the plate or film is first placed in an alkaline developing solution, in which it remains, if *time* development is used, about 5 min. If *stand* development is used, it remains a longer time, 15 to 25 min., in a much less concentrated developing bath. It is then rinsed in water and transferred, usually, to an acid fixing bath. The acidity of this is not very high (pH 4 to 5, see later), but in any case the gelatin has to pass back through the isoelectric point of minimum swelling. Before considering what effect such variations may produce, it will be well to note the order of magnitude of normal swelling with photographic films, and its change with time. Since under normal conditions the gelatin can only swell perpendicularly to the plane of the plate or film, the swelling can be measured either by weighing or by measuring the thickness. In Fig. 5 is shown the rate of swelling of a photographic emulsion followed by *weight*. In this case sodium carbonate solution was used, this being a generally used alkaline component of developers. In Figs. 6 and 7 are illustrated the course of swelling of an emulsion in sodium sulfite solutions, and in a pyrogallic acid developer with sodium sulfite. All these determinations were made by the weighing method. This procedure is time-consuming, and not applicable where it is desired to follow the progress of swelling simultaneously with an actual photographic operation—*e. g.*, development. To accomplish this the writer has designed an instrument to measure the thickness at any stage. This instrument, which may be termed an *auxometer*, is illustrated in Fig. 8. It consists of a micrometer carrying a delicate balance beam; at one end is a silica rod, with a small foot just in contact with the film surface, at the other is a counterpoise. Any increase in thickness (swelling) throws this off balance, the deflection being optically magnified. Balance is restored by

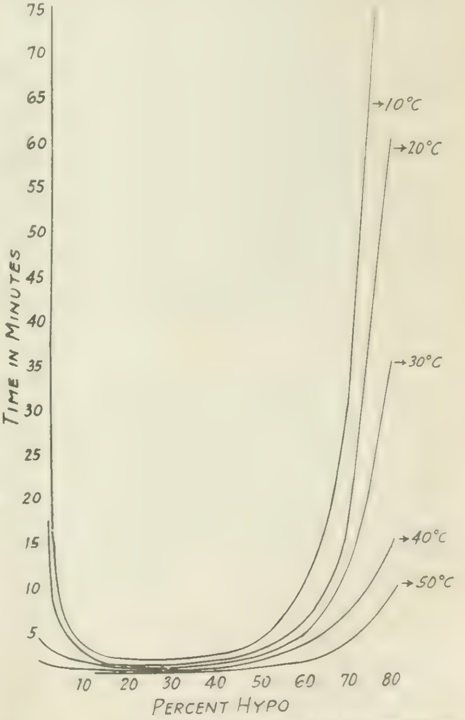

FIG. 10—INFLUENCE OF "HYPO" CONCENTRATION ON TIME OF FIXATION

the micrometer screw, and the change in thickness read. In Fig. 9 is shown the swelling of a film in an acid solution.

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[19] H. R. Procter and J. A. Wilson, *J. Am. Leather Chem. Assoc.*, **11** (1916), 399.

It is not possible here to deal with the data obtained in relation to photographic development. Certain obvious deductions from the data given are, however, of interest. First, it will be seen that gelatin films and emulsions tend to assume, if not an equilibrium, at least a stationary value, fairly rapidly. In solutions of alkaline carbonates and sulfites, although alkaline, the swelling is less, for concentrations above 5 per cent, than in water, and this depressing effect increases rapidly with the concentration of the salt. This effect is taken advantage of in preparing developing solutions for use at high temperatures, as in the tropics. It may be further noticed that the maximum swelling developed with gelatin on rigid supports tends to be considerably less than that obtained, at the same temperature and pH, with gelatin not attached to a rigid support. In the latter case there is some dilation in all directions, whereas the photographic layer can only swell normally to the support. If by any means[20] the swelling is forced beyond the limit compatible with this normal swelling, so that the tangential swelling pressure comes into play, two things may happen—the gelatin may frill and float off the support, or reticulation may occur. This is the production of a network pattern over the film, which spoils the appearance, particularly since the silver particles of the image concentrate in the ridges. Such reticulation is particularly marked after treatment of gelatin with a tanning agent, followed by warm water.

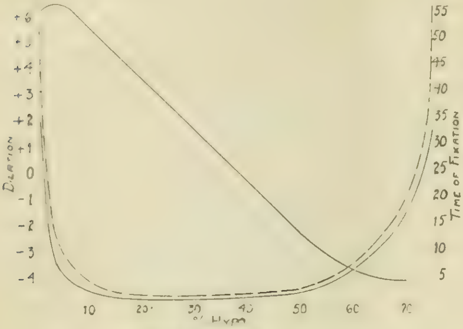


Fig. 11—Influence of Swelling on Time of Fixation

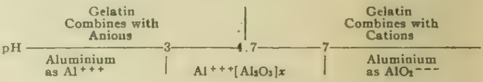
Fixation

The use of an *acid*-fixing bath, primarily to keep down developer stain, involves, as already stated, passage of the gelatin through the isoelectric point of minimum swelling (pH = 4.8). Evidently, if the acidity were considerable, so that pH approached 3–2, the swelling pressure might increase sufficiently to cause trouble. Actually, however, the pH of a fixing bath, containing sodium thiosulfate and sodium sulfite, cannot be much less than 4, for otherwise sulfur would be precipitated. The influence of the swelling factor on the rate of fixation (solution of silver bromide in "hypo" solution) is brought out in Figs. 10 and 11. The time of fixation is a minimum for a concentration of thiosulfate of about 40 per cent, above which it again increases. This is due to the fact that from this point on the reduction of swelling more than compensates for *mass action*.

The relatively anti-swelling, or temporary hardening effect of the acid-fixing bath is generally reinforced by the addition of true hardening (tanning) agents, such as potash alum, chrome alum, or formalin. The hardening action of alums is of great importance photographically, and the writer and his collaborators are making an extended study of the physicochemical conditions. The influence of the H-ion activity, (measured with a hydrogen electrode) on the hardening action of a solution of potash alum ($K_2SO_4.Al_2(SO_4)_3.24H_2O$) is shown in Fig. 12.

The melting points, given as ordinates of the curve, were not determined as noted previously, but directly in water in which the jelly was immersed after it had been soaked a given time in the hardening bath. This corresponds to the conditions in photographic practice. It will be seen that all the solutions give a maximum at the same pH, about 4.0; this was not changed by altering the pH of the gelatin by previous immersion in acid or alkaline solutions. In absence of alum, the maximum occurs at a pH of 4.7 to 4.8, so that the displacement by the aluminium seems definite. From J. Loeb's work on the influence of cations, and specifically of Al^{+++} on the properties of gelatin,[21] it would seem we should anticipate the maximum hardening at a pH > 4.7, for pH > 4.7 gelatin combines only with cations, pH < 4.7, only with anions.

A consideration of the state of aluminium itself in relation to H-ion activity is necessary here, and is roughly indicated in the diagram:



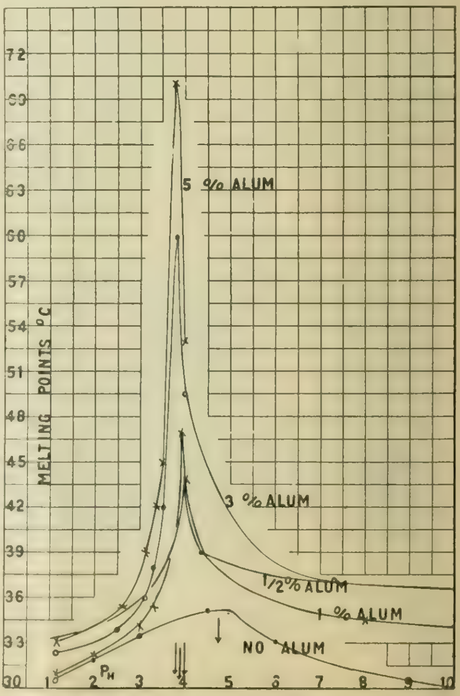


Fig. 12—Influence of pH on Alum Hardening of Gelatin

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[20] S. E. Sheppard and F. A. Elliott, "The Reticulation of Gelatin." This Journal, 10 (1918), [illegible]

[21] *J. General Physiol.*, 1 (1918), 503.

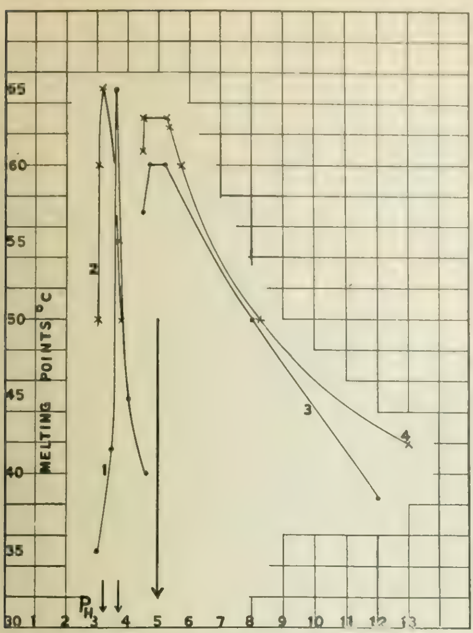

FIG. 13—CURVES 1, 2, 3, 4: 3 PER CENT ALUM AND 0.5 PER CENT CITRIC. CURVES 1, 3: 1 PER CENT SODIUM SULFITE. CURVES 2, 4: 2 PER CENT SODIUM SULFITE. CURVES 3, 4: 25 PER CENT HYPO

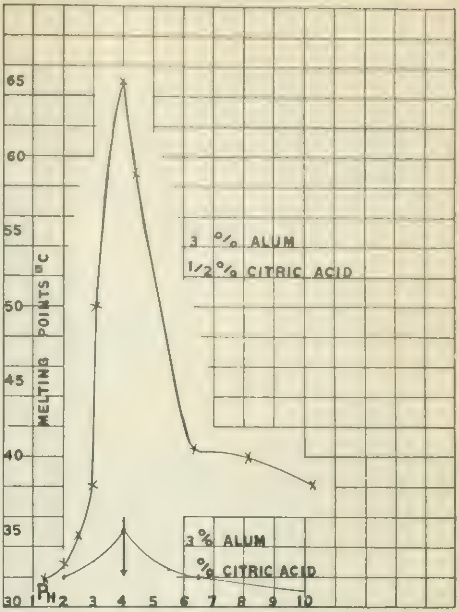

FIG. 14—INFLUENCE OF CITRIC ACID ON HARDENING OF GELATIN BY ALUM (0.5 AND 1 PER CENT CITRIC ACID)

Aluminium commences to precipitate as hydrous alumina, at $pH = 3$; precipitation is complete at $pH = 7$, beyond which alumina goes into solution as aluminates. Between $pH = 3$ and $pH = 7$ there probably exist complexes, of the type $Al^{+++} [Al_2O_3]x$, which are positively charged, and could combine with a negatively charged gelatin ion.[22] The present results point definitely, however, to combination of Al with gelatin at a $pH < 4.7$, and it appears possible that this is a mean value, and that some gelatin capable of combination with cations exists for $pH < 4.7$. We do, however, find that the addition of sodium sulfite and sodium thiosulfate, as used in making an acid-fixing and hardening bath, displaces the pH of maximum hardening to values ≥ 4.7 (Fig. 13). This is possibly due to stabilization of the positively charged Al complexes, and is under investigation. There is another interesting point in this connection. In an acid-fixing bath pH cannot be much less than 4, otherwise *sulfur* will be precipitated from sodium thiosulfate. Yet, if pH is >4, alumina will tend to precipitate and the bath will become useless. This impasse is overcome by using as the acidifier such organic acids as citric, tartaric, etc., which form complexes with aluminium and prevent precipitation by hydroxyl ions. This complex formation lowers the hardening action, as shown in Fig. 14, since the complex formation removes Al^{+++} ions, and it is necessary to increase the alum content to secure effective hardening. Loeb[20] has suggested that the antagonistic effect of citric acid on the combination of gelatin with aluminium is due to its being tribasic, neutralizing a trivalent cation. This is not the case. The antagonistic action is due to the complex formation, and is shown by other monobasic and dibasic organic acids, particularly hydroxy acids. The hardening action of chromium salts is governed by similar conditions, with certain singularities under investigation, and the behavior of dichromated gelatin is closely connected with these tanning reactions. It is now in order to note briefly the operations of *washing* and *drying* gelatin plates and films. Washing out substances, such as "hypo," etc., from gelatin follows in general the law regulating the washing of precipitates. Two things may, however, be noted. On washing out strong electrolytes from gelatin, it will tend to approach the isoelectric point, but if hydrolyzable substances are present, the gelatin will retain unequal amounts of the basic or acidic constituents, the excess depending upon conditions.

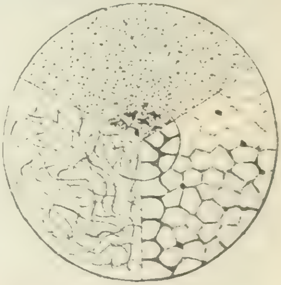

FIG. 15—SUGGESTED STRUCTURES OF GELATIN JELLIES

It has been impossible, in the space at my disposal, to discuss the many important, if incidental, roles played by gelatin in deviations from or developments of the straight process of negative making. Such are the incidents of hydrolysis and oxidation of the gelatin in photographic operations, its capacity for absorption and fixation of dyes, and many others. Again, the simple operation of drying shows interesting features, of which one only may be mentioned as bearing upon the so-called *structure* of gelatin jellies. Fig. 15 illustrates three typical suggested structures—*viz.*, the *honey-*

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[22] The formation of complex aluminium anions may commence earlier.

comb or alveolar, the filamentous, fibrillar, or *felt* structure, and the *granular* structure. Appeal is made to these, variously, to explain certain properties of jellies.[23] In particular, the honeycomb or cell structure has been cited in explanation of the effects of the concentration at setting on the swelling of dried jellies. A jelly at 5 per cent concentration on drying and reswelling again halts at 5 per cent, a 10 per cent one at 10 per cent, etc. It has been suggested that in the more dilute jellies a more open structure of larger cells is formed. In a recent paper the writer and F. A. Elliott[24] have explained this as being a result of external case-hardening. Under ordinary drying conditions a nonuniform drying forms a permanently set skin, conserving the original surface extension of the piece of jelly, and this limits the subsequent dilation on swelling. An internal structure is therefore an unnecessary hypothesis for the explanation of the concentration effect.

[23] "Physics and Chemistry of Colloids." Report of general discussion by the Faraday Society and the Physical Society, London, p. 40. (Department of Science and Industrial Research, Great Britain.)

[24] *J. Am. Chem. Soc.*, **44** (1922), 373. Dr. T. Slater Price, director of the British Photographic Research Association, has called the writer's attention to previous notice of the edge drying of gelatin jellies by R. Liesegang, *Kolloid.-Z.*, **7** (1910), 305; Liesegang, however, does not seem to have related this to the concentration effect.

A New Calculating Chart[1,2]

By E. L. Rice

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Mechanical calculations are of growing importance in industrial and theoretical chemistry, and reliable methods for saving time without a sacrifice of accuracy are much appreciated. We are glad, therefore, to present a new calculating chart, together with rules for its use and examples of its application in the various branches of mathematics.

Our illustration is a reduction from a 34-in. wall chart which in this larger size facilitates following the lines and curves and makes possible calculation at a glance. (Editor.)

THIS CHART accelerates multiplication, division, finding of decimal and metric equivalents, conversion between different units, finding of roots and powers; permits of multiple operations in one, and the solving of any problem in triangulation. The accuracy is of the same order as that of a slide rule, and the device has the added advantage of no movable parts, and the consequent freedom from error due to warping. The full-sized chart has a further commendable feature in that, owing to the individuality of the divisions, most of the operations may be made at a glance, and therefore much more rapidly than can otherwise be done.

The chart is divided into four sets of lines: namely, slant lines, which are factors, and may be divisors, angles, quotients, centimeters, kilowatts, denominators, decimal equivalents, or other factorial elements; radial lines, which are also factors and may perform substantially the same functions as the slant lines; vertical lines, which may be used as products, dividends, lesser sides of triangles, inches in metric conversion, horse-power hours, numerators, the lesser denomination in all conversions, and other functions; two curves running from one lower corner to the other, the upper curve being the cube root curve, which is used to obtain cubes and cube roots, and the lower curve the square root curve, which is used to square numbers and to extract square roots.

Line Divisions

Each of the three sides of the chart is divided into tenths and hundredths, and the slant side and base of the chart are also divided into two-hundredths. The degrees along the left side, under H, are sines of angles from 6 to 90, and are divided into tens and units up to 65. Along the base of the chart, under B, the tangents of angles from 6° to 44° are given and are divided into tens and units. The heavy black lines dividing each side of the chart into tenths are one-one-hundredth wide, and are designated by large numbers set in circles. The thin white lines run through the center of the black lines to the point itself, and the edges of the heavy black lines are each one-two-hundredth distant from the point, so that at large number 4, for instance, the edges of the black line fall on 395 and 405.

Division

To divide, follow the vertical line, which is the dividend, and locate where it crosses the given sum as a divisor, which may be either the slant or the radial, and read the quotient upon either of the two factor lines; that is to say, if the divisor is the radial, read the quotient upon the slant, and if the divisor is slant, read the quotient upon the radial. Thus, for illustration, given a simple problem of 56 divided by 8. Notice the diamond midway between large 5 and 6, and next to this at the right, the line from the 6 point, which is the line representing 56. Follow the vertical line from this point to where it crosses the slant line 8 and notice that it is exactly on the radial line 7, and therefore the answer or quotient is 7 (Fig. 2[3]). Now if you wish to divide 565 by 8, simply read a little further over, midway between the 6 and 7 lines to the right of large 5, and read the quotient as 70.6. Thus, the simple rule for division is to follow the vertical for the dividend to the point of intersection of either a radial or slant for the divisor, and read the quotient upon the other of either the radial or slant.

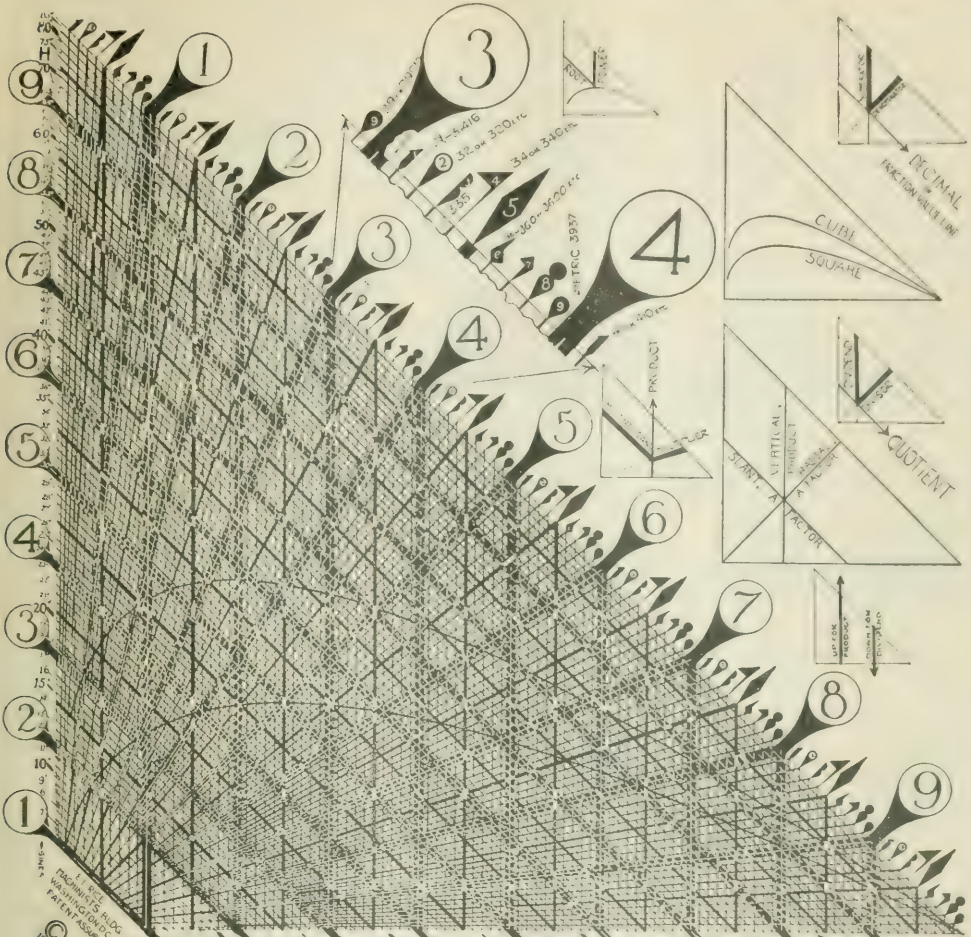
Multiplication

In multiplication the process of division is reversed—that is, the vertical is the product and the slant and radial are the two factors. It is immaterial whether the radial or the slant is used for the multiplier, although it is preferable to read the factor having the greater number of digits from the top, as the graduations are both wider and more easily read by reason of the legends at the ends of the lines. Thus in multiplying, all that is necessary is to find the intersection of a slant and radial representing the two numbers and read the product upon the vertical. For instance, 8 radial crosses 7 slant at 56 vertical (Fig. 3). Again, if there are two digits to each number, say 45 times 45, the two cross nearly upon the vertical 2 line, and the answer is approximately 2000, or exactly 2025. Now if you have 455 multiplied by

[1] Received October [illegible], 1922.

[2] Copyright 1922, E. L. Rice.

[3] See page 1034 for Figs. 1 to 29.



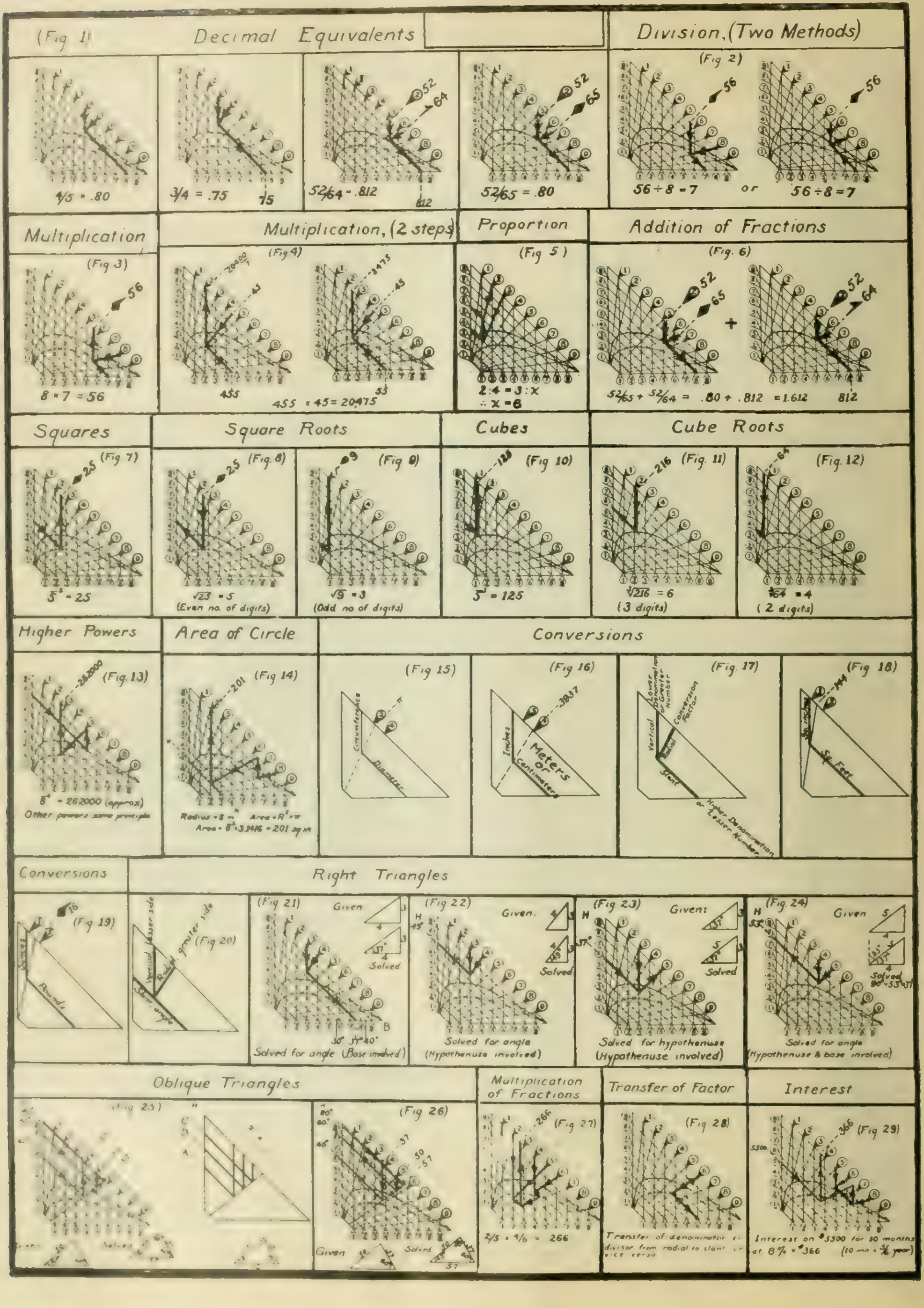
45, perform the operation in two steps. In the first step multiply the given numbers and read the product as approximately 20,400, since you can read the first three digits correctly from the chart. In the second step multiply the last two digits of each of the given numbers, that is, multiply 55 by 45, and read the answer as 2475, since you can read the first three digits correctly and you know that the last digit is 5, because the last digit of each of the factors is 5. Then the last two digits of this second product are the correct fourth and fifth digits of the first product, so you know that 455 multiplied by 45 equals 20,475 (Fig. 4). That is to say, by the first multiplication the first three digits are positively determined, and by the second multiplication the last two digits are positively determined, so that by combining operations you can multiply to five digits with accuracy upon this chart.

Squares

In order to square a number, follow either a radial line or a slant line until it crosses the square root curve—the lower curve—and read the answer on the vertical. For instance, to square 5, follow either the radial 5 or the slant 5 to the lower curve and you will find that they cross on this curve; by following the vertical line through this point of intersection the square of 5 to be 25 is found (Fig. 7).

Square Roots

If you desire to extract the square root, reverse the process; for example, assuming that you desire to extract the square root of 25, follow the vertical from the diamond midway between the large 2 and 3, to where it crosses the square root curve and read the answer of 5 either on a radial or a slant


(Fig 1) Decimal Equivalents
4/5 = .80
3/4 = .75
75
52/64 = .812
812
52/65 = .80
Division, (Two Methods)
(Fig 2)
56 ÷ 8 = 7 or 56 ÷ 8 = 7
Multiplication
(Fig 3)
8 × 7 = 56
Multiplication, (2 steps)
(Fig 4)
455 × 45 = 20475
Proportion
(Fig 5)
2 : 4 = 3 : x
∴ x = 6
Addition of Fractions
(Fig. 6)
52/65 + 52/64 = .80 + .812 = 1.612
Squares
(Fig 7)
5² = 25
Square Roots
(Fig. 8)
√25 = 5
(Even no. of digits)
(Fig 9)
√9 = 3
(Odd no of digits)
Cubes
(Fig 10)
5³ = 125
Cube Roots
(Fig. 11)
∛216 = 6
(3 digits)
(Fig. 12)
∛64 = 4
(2 digits)
Higher Powers
(Fig. 13)
8⁶ = 262000 (approx)
Other powers same principle
Area of Circle
(Fig 14)
Radius = 8 in. Area = R² × π
Area = 8² × 3.1416 = 201 sq in
Conversions
(Fig 15)
Circumference
Diameter
(Fig 16)
Inches
Meters or Centimeters
(Fig. 17)
Vertical
Lower Denomination or Greater Number
Conversion Factor
Slant
Higher Denomination or Lesser Number
(Fig 18)
Sq. Inches
Sq. Feet
Conversions
(Fig 19)
Pounds
Right Triangles
(Fig 20)
Vertical lesser side
Radial
greater side
Slant angle
(Fig 21)
Given
Solved
Solved for angle (Base involved)
(Fig 22)
Given.
Solved
Solved for angle (Hypothenuse involved)
(Fig 23)
Given:
Solved
Solved for hypothenuse (Hypothenuse involved)
(Fig. 24)
Given
Solved
Solved for angle (Hypothenuse & base involved)
Oblique Triangles
(Fig 25)
Solved
(Fig 26)
Given
Solved
Multiplication of Fractions
(Fig 27)
2/5 × 4/6 = .266
Transfer of Factor
(Fig 28)
Transfer of denominator or divisor from radial to slant or vice versa
Interest
(Fig 29)
Interest on $5500 for 10 months at 8% = $366 (10 mo = 5/6 year)

(Fig. 8). It will be noted at this time that there are two different square roots of every like set of numbers—that is, 25 has one root, 2.5 has another root—which are entirely distinct. In finding square roots, numbers having an even number of digits to the left of the decimal point are read on the scale to the right of large 1; numbers having an odd number of digits are read on the scale to the left of large 1.

Cubes

To find the cube of a number, follow the slant line of the given number until it crosses the cube curve, which is the upper curve, and follow the vertical line for the answer. Thus, the cube of 5 is found by following the slant line 5 until it crosses the cube curve, and reading the answer of 125 on the vertical line (Fig. 10). Do not try to cube or extract the cube root by reading the radial. Either the radial or the slant can be used for the square and square root, but not for the cube and cube root.

Cube Roots

In cube roots, separate the number into groups of three digits to the left of the decimal point, and if the left-hand group has three digits, then follow a vertical line on the scale to the right of large 1 until the vertical crosses the cube curve, and the slant gives the answer; if the left-hand group has two digits, locate the vertical line on the scale to the left of large 1; if there is but one digit in the left-hand group, the vertical line is located between zero and the 1 line to the left of large 1.

Higher Powers

Numbers can be raised to higher powers by combinations of the square curve and the cube curve. For example, to raise a number to the sixth power, follow the slant of the number to the cube curve, follow the vertical from this point to the top, then follow the radial from this last point to the square curve, and follow the vertical to the top, where the answer may be read.

Right Triangles

In trigonometric calculations this chart solves practically any problem that can be solved after a year's study of trigonometry, and the solution is much more rapid. A simple rule to remember in right triangle calculations is that the vertical is the lesser side and the radial is the greater side, and the angle is read upon the slant line through the intersection of the vertical and the radial (Fig. 20). It will be noted that at the left of the chart, under H, there is a series of graduations indicating degrees (sines), and at the base of the chart, under B, there is another set of graduations in degrees (tangents). In right triangle calculations, those under H are used if the hypotenuse is involved as a given or desired quantity, and those under B are used when the base is involved, and the hypotenuse is not. When both the base and hypotenuse are involved, the graduations under H are used, and the angle read is subtracted from 90° to obtain the angle included between the base and hypotenuse of the given triangle. It makes no difference which two sides of a right triangle are given; first observe which is the greater and which is the lesser side, follow the vertical of the lesser until it crosses the radial of the greater, and the slant line, through the point of intersection, gives the angle. If the angle is determined from the H scale, as described above, it is the angle between the base and hypotenuse of the triangle; if determined from the B scale it is the smallest angle of the triangle. If the angle is given and the greater side is given, follow the radial of the greater side until it crosses the slant of the angle, and the vertical will give you the lesser side. For example, given a base of 4 and an altitude of 3, find the smallest angle of the triangle; follow the vertical 3 to where it crosses the radial 4, and follow the slant from this point to the scale at the bottom of the chart, since in this problem the base of the triangle is involved, and the angle is found to be approximately 37° (Fig. 21).

Oblique Triangles

In the solution of oblique triangles, if a side and its opposite angle are not given, break it up into right triangles and solve. If a side and its opposite angle are known, follow the slant of the angle to where it meets the vertical of the opposite side and locate the radial through this point; then each angle will intersect its opposite side on this same radial. In this solution the verticals always represent the sides, and the angles are always read under the H scale, because from geometry these angles are the only functions that have the same ratio as the opposite sides. For example, given an oblique triangle having one angle of 40°, another angle of 60°, and a side of 50 opposite the last given angle. Since you know two angles, find the third by subtracting the sum of 40° and 60° from 180°, which is 80°. Now follow the 60° slant to where it crosses the 50 vertical line, follow the radial through this point to where it crosses the 40° slant, and read the vertical through this last point to obtain the side opposite the 40° angle; this side will be found to be approximately 37. Now follow along the same radial mentioned to where it crosses the 80° slant line, and the vertical through this point gives the side opposite the 80° angle; this last side will be approximately 57 (Fig. 25).

Condensed Rules

Arithmetic

Multiplication—Slant and radial lines are factors; vertical is product. Either factor may be multiplier and the other multiplicand (Fig. 3).

Division—Vertical is dividend; either slant or radial may be divisor and the other slant or radial the quotient (Fig. 2).

Factoring—Lines intersecting on the vertical are its factors. All factors are determined at a glance by running the eye down the vertical. Factoring, however, is now useless, as addition and subtraction of fractions are done at a glance without the necessity of finding the L. C. M. or G. C. D.

Fractions—Common fractions preferably read with vertical as numerator, radial as denominator, and slant as quotient or decimal equivalent (Fig. 1).

Addition and Subtraction—Read decimal equivalent on slant, and add or subtract decimals (Fig. 6).

Multiplication—Follow slant through intersection of vertical numerator and radial denominator of one fraction to square root curve, and follow radial from square root curve to intersection of slant from other fraction; read product on vertical. Square root curve transfers decimal from slant to radial and thereby multiplies the two decimals (Fig. 27).

Division—Follow slant of dividend fraction to base of chart and vertical from there to intersection of slant decimal of divisor; read quotient on radial.

Proportion—The means and extremes intersect on the same vertical (Fig. 5).

Interest—Months given, read 6ths of year; thus 4 mo. equals 2/6, 5 mo. equals 2.5/6. Days given, read vertical of number of days over intersection of 365 radial. This determines slant. Follow slant until it intersects radial of rate of interest. Follow vertical from this intersection to top and back on radial to slant of given sum. Read answer on vertical (Fig. 29).

CONVERSIONS—Read lower denomination or greater number on vertical, and higher denomination or lesser number on slant over conversion factor (Fig. 17); thus, days on vertical and years on slant through intersection of vertical and radial conversion factor 365.

ROOTS AND POWERS—Square and cube roots and powers read directly from square and cube curves. Either radial or slant is factor in square roots and powers. Slant only is cube root (Figs. 7 to 12).

Higher Powers—5th power: read to square curve twice and then to root line. 6th power: to cube and then to square curve (Fig. 13). 7th power: to cube curve, then to square curve, and then to root line. 8th power: to cube curve, to square curve, and to root line twice.

ALGEBRA

Resolve fractions as in multiplication and division of fractions and resolve equations as in proportion.

GEOMETRY

CIRCLES, SPHERES—Read circumference on vertical and diameter on slant over radial π line (Fig. 15).

AREA OF CIRCLE—Radial radius to square curve, then up vertical and down radial to slant π line; answer on vertical from π (Fig. 14).

TRIGONOMETRY

RIGHT TRIANGLES—Vertical is lesser side, radial is greater side, slant is angle. Read B angles if base is involved as given or desired quantity, H angles if hypotenuse is involved, H complementary angles if both base and hypotenuse are involved. Hypotenuse always the greater side. Base greater than altitude under 45°, and lesser over 45° (Figs. 20 to 24).

OBLIQUE TRIANGLES—All angles and their opposite sides intersect on the same radial; angles under H are read. If side and opposite angle are not given, break into right triangles (Figs. 25 and 26).

A Simple Graphical Method of Calculating the Number of Plates Required for a Distilling Column[1]

By W. H. Rodebush[2]

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IN HIS recent book on distillation,[3] Clark S. Robinson treats the theory of a continuously operated column by a method developed by W. K. Lewis. This method appears somewhat involved and is strictly applicable to a column with an infinite number of plates. Now the rectification in an ordinary continuously operated column with a limited number of plates is a step-by-step process from plate to plate, and the following method of treatment, while not essentially different, appears simpler and more exact.

Let the rate of flow be expressed in mols per unit time and the composition by the mol per cent of the more volatile constituent. Following the notation of Robinson, let V_b be the rate of flow of the vapor of composition y_b upward from plate b, R_b the rate of reflux of liquid of composition x_b downward from the same plate, and V_c be the output of composition y_c from the top of the column per unit time.

From an inspection of Fig. 1 the conditions to be satisfied for a steady operation of the column are readily set down. The first condition is that the liquid leaving any plate, as b, for the plate below, is in equilibrium with the vapor leaving this same plate for the plate above. This is, of course, a limiting condition reached only with a column which is functioning perfectly, but it may be approached in a column properly designed and operated, and deviations from this condition may be corrected by allowing a constant factor for imperfect performance. This condition may be expressed mathematically by the equation

$$y_b - x_b = l \qquad (1)$$

where l is the difference between vapor and liquid composition when the two phases are in equilibrium. In Fig. 2, l is plotted as ordinate against x, the liquid composition for benzene and toluene. The data used are those obtained by Rosanoff.[4] This diagram is fundamental in calculating the conditions necessary for the separation of two liquids, and, where the data are not to be found in the literature, they may be obtained in a few hours in the laboratory with sufficient accuracy by distilling in an ordinary distilling flask small portions successively from a large amount of liquid whose composition varies slowly, and determining the composition of distillates and residues.

In addition, the two following equations given by Robinson hold for any cross section of the column as s in Fig. 1.

$$V_a - R_b = V_c \qquad (2)$$

$$V_a y_a - R_b x_b = V_c y_c \qquad (3)$$

Solving these equations,

$$x_b = y_a - (y_c - y_a)\frac{V_c}{R_b} \qquad (4)$$

Suppose the vapor entering the column above plate a has the composition y_a. For an infinite amount of reflux or zero output, the last term in Equation 4 becomes zero and we have $x_b = y_a$. This value is obtained geometrically (Fig. 2) by measuring off with a pair of dividers the distance l_a along x from x_a. By repeating this process of laying off l_n along x from x_n until y_c is reached, we get the minimum number of plates for infinite reflux, each measurement corresponding to a plate.

Of more practical significance is the limiting ratio of output to reflux possible when the number of plates is infinite. If the number of plates is very large, the composition of liquid varies but slightly from plate to plate and in the limit $x_a = x_b$. Hence Equation 4 becomes:

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[1] Received April 24, 1922.

[2] Associate Professor of Physical Chemistry.

[3] "Elements of Fractional Distillation." McGraw-Hill Book Co., 1922.

[4] *J. Am. Chem. Soc.*, **36** (1914), 1999.

$$x_a = y_a - (y_c - y_a)\frac{V_c}{R_b} \qquad (5)$$

or

$$\frac{V_c}{R_b} = \frac{l}{y_c - y_a} \qquad (6)$$

Owing to the approximate validity of Trouton's rule for heat of vaporization, the vapor and liquid flows will not vary appreciably from plate to plate throughout the column for liquids whose boiling points are not far apart.[5] A constant reflux throughout the column being assumed, the actual ratio V_c/R will be fixed by the plate in the column where $\frac{l}{y_c - y}$ is a minimum. That is to say, the output of any constituent per unit time cannot be greater than the net amount of that constituent which rises past any plate in the same time. $\frac{l}{y_c - y}$ will be a minimum at the point on the diagram (Fig. 3) where the angle yy_cx is a minimum.[6] The limiting ratio V_c/R having been determined by this method for an infinite number of plates, the number of plates actually required in a working column may be calculated graphically by the following modification of the method described above.

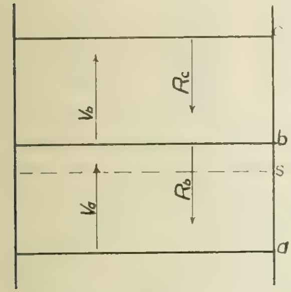

Fig. 1

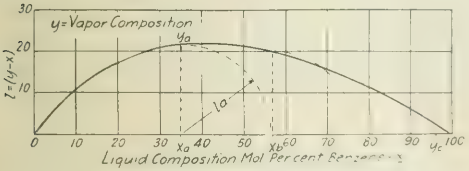

Fig. 2—Benzene-Toluene

In Fig. 3 we have the vapor-liquid composition diagram for ethanol and water according to the data given by W. K. Lewis.[7] Let the vapor entering the column be of composition y = 46.5 per cent, the output y_c = 86 per cent. Then the limiting ratio of $\frac{V_c}{R}$ for an infinite number of plates is given by $\frac{l}{y_c - y}$ at the point x = 78 per cent, where the angle $y_n y_c x_n$ is a minimum. Here $\frac{V_c}{R} = \frac{1}{3}$ (approximately).

Assume now a working ratio $\frac{V_c}{R} = \frac{1}{7}$. Proceed as above to find the point $x = y_a$ = 46.5 per cent. Now from Equation 5, $x_b = y_a - (y_c - y_a)\frac{V_c}{R}$, x_b is evidently to the left of the point $x\ (= y_a)$ by the amount $(y_c - y_a)\frac{V_c}{R}$. $(y_c - y_a)$ is the distance from y_c to the point $x = y_a$. Then x_b will lie at the distance $\left(1 + \frac{V_c}{R}\right)(y_c - y_a)$ from y_c or $\frac{8}{7}(y_c - y_a)$. Draw a line y_cz at such an angle with the x axis that its secant is $\frac{8}{7}$. Then with a pair of dividers lay off a distance from y_c on the x axis equal to the distance y_cz1 where $z1$ is the intersection of y_cz with the perpendicular to the x axis at $x = y_a$. Then x_b will be at the point located. The proof is obvious by geometry.

The process is then repeated, starting with y_b the composition of vapor in equilibrium with x_b, and continued until y_c is reached. Each construction corresponds to a plate in the column. Approximately 15 plates are indicated by this method as necessary to produce 86 per cent alcohol[8] from 46.5 per cent with a ratio of output to reflux of 1 to 7.

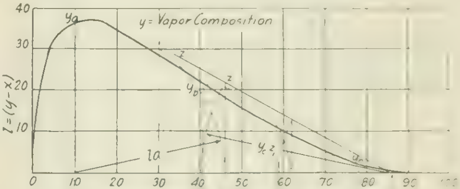

Fig. 3—Ethanol Water

The foregoing applies only to the upper portion of the column above the entering vapor. For the lower portion of the column similar equations may be derived. If liquid is being drawn off from the bottom of the column at a rate $V_o = V_a - V_c$ of composition $x_o = \frac{V_a y_a - y_c V_c}{V_o}$, then if r and s be successive plates proceeding downward in the column,

$$y_s = x_r + (x_r - x_o)\frac{V_o}{R} \qquad (7)$$

or

$$y_s - x_o = \frac{1}{1 - \frac{V_o}{R}}(x_r - x_o) \qquad (8)$$

If R is assumed to be constant throughout the whole column, the number of plates in the lower portion may be determined graphically on the vapor composition diagram by a method precisely similar to that employed for the upper portion.

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[5] This generalization can only be applied satisfactorily to those liquids which Hildebrand has called *normal liquids*. [*J. Am. Chem. Soc.*, **37** (1915), 970.] Water and ethanol differ markedly from the normal liquids but their values for the molal heats of vaporization do not differ from each other enough to invalidate the above approximations for alcohol-water mixtures. W. A. Peters, Jr., has suggested expressing the composition in units of equal heat of vaporization instead of mols. This would solve the problem quite satisfactorily except in the case of a substance such as acetic acid, which has an abnormal vapor density that varies with temperature and pressure. The heat of vaporization is likewise a variable quantity and the composition would have to be expressed in a variable unit.

[6] It can be shown mathematically that $\frac{l}{y_c - y}$ is a minimum when $\frac{l}{y_c - y + l}$ is a minimum; but $\frac{l}{y_c - y + l}$ is the tangent of the angle yy_cx. Hence $\frac{l}{y_c - y}$ is a minimum when the angle yy_cx is a minimum.

[7] This Journal, **12** (1920), 496.

[8] It should be remembered that the compositions are in mol per cent. 86 mol per cent composition is equivalent to 94 per cent by weight

Relation of Hydrogen-Ion Concentration to Filter-Plant Operation[1]

By William D. Hatfield

WATER DEPARTMENT, CITY OF HIGHLAND PARK, MICHIGAN

It is known that the pH value of a solution is a controlling factor in precipitating and filtering gelatinous materials. The work reported below was undertaken to find that pH value at which best results in coagulation, sedimentation, and filtration were obtained under the conditions of operation of the Highland Park, Mich., filtration plant. When similar data have been collected on numerous plants operating under different conditions, the value of the pH determination to operation will become more definite.

MODERN chemistry is aiding the waterworks chemist and engineer to a new and more accurate idea regarding the coagulation of waters with sulfate of aluminium. The alkalinity of a water exists in two forms: (1) the hydrogen-ion concentration or pH value, and (2) the reserve alkalinity, which is the buffer value of the water. The latter has been determined as the methyl orange alkalinity, while the former is the value which apparently controls the complete precipitation of aluminium from solution.

Experiments in other fields of chemistry have shown that the pH value of the solution is a controlling factor both in the precipitation and filtration of gelatinous materials. If it should be found possible to determine the proper pH value for the coagulation and filtration of a particular water, we should have a simple method for controlling the alum treatment. In case of waters with high alkalinity, it may be economical to reduce the alkalinity by the addition of sulfuric acid and thereby make a considerable saving in alum.

Colorimetric methods for the determination of pH values of water using the buffer solutions of Clark and Lubs[2] or Sorenson[3] are most accurate for the trained chemist with good laboratory facilities, but the author highly recommends the Gillespie[4] method, "without buffers," for the average waterworks laboratory. After the color standards are made up by the chemist, an operator with average intelligence can be taught that 5 or 10 ml. of the mixing chamber water plus a certain number of drops of an indicator should have a certain color when matched with the standards.

Before beginning the experiments on the operation of the plant, preliminary laboratory tests were made on the precipitation of aluminium hydroxide from a solution of filter alum, and on the coagulation of artificially prepared waters. Titration curves of an alum solution (0.855 g. per liter) were made with 0.1 *N* and 0.01 *N* sodium hydroxide, sodium bicarbonate, sodium carbonate, ammonium, and calcium hydroxide. These curves show approximately the same deflection with the central point in the drop of the curve at a pH of 7.0.

The data in Table I were obtained by treating 500 ml. of the samples of waters in beakers with quantities of alum varying from 0 to 3.0 grain per gal. The waters were prepared from distilled water, with fuller's earth for turbidities, and sodium bicarbonate for bicarbonate alkalinities. A freshly prepared alum solution (0.855 g. per liter) was used. One milliliter of this solution in 500 ml. of water is equivalent to 0.1 grain per gal.

The data in Series I, Table I, show that the quantity of alum necessary to produce a clear-cut floc is not dependent on the turbidity, and that in each case good flocculation began at a pH value of from 7.6 to 7.8. It does not necessarily follow that in the operation of a filter plant, where other factors as sedimentation enter, more alum floc will not be necessary to adsorb the higher turbidities.

The data in Series II and III, Table I, show that the quantities of alum necessary to produce a clear-cut floc are dependent on the methyl orange alkalinity and not on the turbidity. As in Series I, good flocculation in each case began at a pH of from 7.6 to 7.8. This means that in cases of high alkalinity large amounts of alum have to be used, not as a coagulant, but to neutralize the alkalinity of the water and bring the pH value down to 7.6 to 7.8, where flocculation begins. The truth of this statement is shown from the data in Series II*a*, Table I. The sample of water used was No. 4 of Series II, which had a turbidity of 45 p. p. m. and a methyl orange alkalinity of 210 p. p. m. The original pH value of the water was greater than 9.0. Sulfuric acid was added to the water until the pH reduced to 8.2. Alum solution was then added to a series of 500 ml. samples in quantities from 0 to 3.0 gr. per gal. Good flocculation took place with from 0.75 to 1.00 gr. per gal. alum, again at a pH of 7.6 to 7.8. This same water, before treatment with acid, required 2.75 gr. per gal. of alum for flocculation.

TABLE I

Sample	Turbidity	Methyl Orange Alkalinity as $CaCO_3$	Gr. per Gal. Alum to Coagulate Sample	pH of Treated Water at Which a Good Floc First Appeared
		Series I—Methyl orange alkalinity constant, turbidity variable		
1	25	111	1.50	7.6 to 7.8
2	75	111	1.50	7.6 to 7.8
3	150	111	1.50	7.6 to 7.8
4	300	111	1.50	7.6 to 7.8
5	600	111	1.50	7.6 to 7.8
		Series II—Turbidity constant, methyl orange alkalinity variable		
1	45	55	0.75	7.6 to 7.8
2	45	107	1.25	7.6 to 7.8
3	45	158	2.00	7.6 to 7.8
4	45	210	2.75	7.6 to 7.8
		Series IIa—Sample 4, Series II, treated with H_2SO_4 to pH of 8.2		
1	45	..	0.75 to 1.00	7.6 to 7.8
		Series III—Turbidity constant, methyl orange alkalinity variable		
1	150	23	No floc	(7.4)[1]
2	150	85	1.00	7.6 to 7.8
3	150	136	1.50	7.6 to 7.8
4	150	218	3.00	7.6 to 7.8

[1] 7.4 was the pH value of the untreated water. 0.25 gr. per gal. of alum brought the pH to 7.1, but in no case was there a floc formed.

In Table II data are given on the treatment of a water having a turbidity of 85 p. p. m. and a methyl orange alkalinity of 112 p. p. m. A good, clear-cut floc which settled readily was obtained between the pH values of 7.6 and 6.6 with applications of alum from 1.5 to 6.0 gr. per gal. Below the pH value of 6.45 the floc became feathery and did not settle. The pH limits, within which the floc coagulated and settled satisfactorily, coincide with those of Blum[5] for the complete precipitation of aluminium hydroxide. It is possible, however, that the complete precipitation of the aluminium also takes place at pH values much lower than the limits given above.

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[1] Presented before the Division of Water, Sewage, and Sanitation at the 63rd Meeting of the American Chemical Society, Birmingham, Ala., April 3 to 7, 1922.

[2] *J. Bact.*, 2 [illegible]; Clark, "The Determination of Hydrogen-Ion Concentration," Williams and Wilkins, 1920.

[3] *Biochem. Z.*, 24 [illegible]; Levy, *Arch. Internal Med.*, 16 (1915), 389; Hawk, "Practical Physiological Chemistry," 5th ed., p. 289, P. Blakiston's Son & Co.

[4] *Soil Science*, 9 (1920), 115; *J. Am. Chem. Soc.*, 42 (1920), 743.

[5] *J. Am. Chem. Soc.*, 35 (1913), 1499.

TABLE II

(Sample of water used: alkalinity 112 p. p. m., turbidity 85 p. p. m.[1])

Alum Added in Gr. per Gal.[2]	Character of Coagulation	Sedimentation	pH Value of Solution
0.0	....	....	8.4
0.5	....	....	8.2
1.0	....	....	7.8
1.5	Good	Good	7.5
2.0	Good	Good	7.4
3.0	Good	Good	7.0
4.0	Heavy	Good	6.8
5.0	Heavy	Good	6.7
6.0	Very heavy	Good	6.6
7.0	Not clear cut	Fair	6.45
8.0	Feathery	Poor	6.35
9.0	Feathery	Very poor	6.3
10.0	Feathery	Very poor	6.25
11.0	Feathery	Very poor	6.15

[1] The solution used was made by addition of sodium bicarbonate and fuller's earth to distilled water.

[2] Further addition of alum solution gradually peptized the feathery flock until the solution showed a deep turbidity only.

The chemical composition of the raw water for the Highland Park supply, taken from Lake St. Claire, is practically constant the year around. Rains have little or no effect on the turbidity and alkalinity, though high winds cause the turbidity to rise from the usual 5 to 20 p. p. m. to 100 to 200 p. p. m. These periods of high turbidity last only a few days. The bacterial content to the water ranges as follows:

Agar 37° 10 to 1000 organisms per milliliter
Agar 20° 100 to 15,000 organisms per milliliter
(*B. coli* average, 6 organisms per 100 ml.)

Because of this constancy of chemical composition and the ease of handling the bacteriological purification, it is possible to run the plant for a month at a definite alum treatment and study the relation of pH values to the efficiencies of coagulation, sedimentation, and filtration, without worrying about changes in alkalinity or sudden gross pollution of the raw water. The raw water has a methyl orange alkalinity of 83 p. p. m. The pH value of the water in the summer months is as high as 8.4 and gradually decreases with temperature until at 1° C. it is 7.8. This gradual lowering may be due to the increased content of carbon dioxide in the water during the winter months.

Table III contains data on the coagulation and pH values of the treated water collected at the end of the mixing chamber when different amounts of alum were added. The same results have been obtained in laboratory beaker experiments. Coagulation takes place at a pH of 7.6, confirming the data on the artificially prepared water. In all experiments it is noticeable that flocculation in beakers requires considerably more time than in the mixing chamber. The reason for this has not been ascertained. It is probably due to a number of differing factors, as stirring, volume, presence of floc nuclei, concentration of alum solution added, etc.

TABLE III

Alum Added Gr per Gal	pH Value of Treated Water	Character of Floc at End of Mixing Chamber
0.0	8.4	None
0.2	8.2	None
0.3	8.0	Very faint
0.4	7.8	Faint
0.5	7.65	Poor
0.6	7.6	Fair
0.63	7.6−	Good
0.69	7.55	Large
0.77	7.4+	Large
0.81	7.4	Large
0.88	7.4−	Large
0.95	7.3	Large
1.01	7.2	Large
1.19	7.15	Large

TABLE IV—COAGULATION OF RAW WATER IN BEAKERS JANUARY 1[illegible] 1922
ORIGINAL TEMPERATURE 1.0° C.

(Last column contains data on the floc in influent to filters in February 1922 showing comparison to beaker experiments)

Alum Added in Gr. per Gal.	pH Value of Treated Water	Time to Form Floc in Beakers	Floc in Influent
0.0	7.8	None in 3 hrs.	None
0.2	7.65	None in 3 hrs.	Very few small particles of floc
0.4	7.6	None in 3 hrs.	Considerable minute particles of floc
0.5	7.4	Fair floc in 3 hrs	Large quantity of fair-sized floc
0.8	7.35	Good floc in 1 hr	Excellently coagulated and settled
1.0	7.2	Good in 30 min.	Excellently coagulated and settled
1.25	7.2−	Good in 30 min.	Excellently coagulated and settled
1.50	7.05	Good in 3 min. Heavy in 30 min	Excellently coagulated and settled

At winter temperatures the pH values of the treated water, as well as the raw water, are lowered as is seen on comparing Tables III and IV. The time of reaction, both in beakers and in the mixing chamber, is prolonged. The last column in Table IV shows that coagulation takes place after the water leaves the mixing chamber, and also shows the point where good sedimentation takes place. Although the initial pH of the raw water is 0.6 lower in the winter than in the summer, as the alum treatment approaches 1.0 gr. per gal., the pH values approach 7.2 both for winter and summer.

Table V contains data on the operation of the filter plant from August 1, 1921, to January 14, 1922. The data on the hours of filter service are reliable and best indicate the efficiency of operation. The data on removal of bacteria expressed by percentage are of less value because the raw water count is often very low. Table V shows that under the conditions of

TABLE V—DATA ON THE OPERATION OF HIGHLAND PARK FILTER PLANT BEFORE CLEANING SEDIMENTATION BASIN
(August 1, 1921, to January 14, 1922)

Dates	No. of Days	Temp. °C.	Turbidity	Alum in Gr. per Gal.	pH Value Raw Water	pH Value Treated[1] Water	Per cent Bacterial Efficiency of Sedimentation 20°	Per cent Bacterial Efficiency of Sedimentation 37°	Per cent Bacterial Efficiency of Filtration 20°	Per cent Bacterial Efficiency of Filtration 37°	Average Hrs. of Filter Service Coarse Sand	Average Hrs. of Filter Service Fine[2] Sand	Per cent Wash Water Used	Cost of Treatment per Million Gallons
Aug. 1 to 17, Sept. 13 to 16, 1921	21	28	10	0.60	8.4	7.6	..	(83)	.	(92)	31	22	1.72	$1.81
Sept. 17 to Oct. 20, 1921	34	20	16	0.68	8.0	7.5	..	68		81	36	27	1.35	1.87
Oct. 22 to Nov. 25, 1921	36	12	31	0.78	8.0	7.4	59	67	87	87	46	33	1.15	2.02
December 1 to 31, 1921	31	4	19	0.92	7.8	7.3	61	73	90	97	58	40	1.02	2.28
January 5 to 13, 1922	9	1.5	11	1.07	7.8	7.2	..	52		97.5	52	35	1.09	2.56
January 14 to 17, 1922	4	1.5	15	1.19	7.8	7.15	48	43	90	98.5	46	33	1.11	2.83

[1] pH values have been run on raw, mixed, settled, filtered, and chlorinated waters. The pH values of the last four are always identical as collected at this plant.

[2] Eight of the filter beds are made of a coarse Red Wing sand and four are made of a finer Cape May sand. The bacterial efficiencies of the two sands are about the same, but the fine sand gives fewer hours of service.

TABLE VI—DATA ON THE OPERATION OF THE HIGHLAND PARK FILTER PLANT AFTER CLEANING SEDIMENTATION BASIN
(February to April 1922)

Dates	No. of Days	Temp. °C.	Turbidity	Alum in Gr. per Gal.	pH Value Raw Water	pH Value Treated Water	Per cent Bacterial Efficiency of Sedimentation 20°	Per cent Bacterial Efficiency of Sedimentation 37°	Per cent Bacterial Efficiency of Filtration 20°	Per cent Bacterial Efficiency of Filtration 37°	Average Hrs. of Filter Service Coarse Sand	Average Hrs. of Filter Service Fine Sand	Per cent Wash Water Used	Cost of Treatment per Million Gallons
February 14 to 23, 1922	10	1.5	3	0.21	7.8−	7.7	0	0	74	70	67	46	0.80	$0.69
February 24 to March 3, 1922	8	2.0	8	0.42	7.8	7.6	15	26	88	98	55	35	0.89	1.17
March 4 to 11, 1922	8	2.0	12	0.62	7.8−	7.4−	23	21	81	86	58	37	1.34	1.73
March 12 to 19, 1922	8	2.5	17	0.75	7.8	7.3−	64	55	95	96	61	46	0.99	1.89
April 13 to 16, 1922	4	8.0	24	0.95	7.9−	7.2	85	83	95	98	65	47	0.70	2.45

operation of this plant the most efficient results were obtained with an alum dosage of 0.9 gr. per gal. and the pH of the treated water at 7.3. Larger amounts of alum, though slightly increasing the bacterial efficiency, decreased the hours of service of the filters and increased the wash water. Fluctuations in turbidity up to 195 p. p. m. were handled at pH values from 7.3 to 7.4 without difficulty.

During the course of these experiments the tap water at all times conformed to the Treasury standards, even though only 0.05 to 0.18 p. p. m. chlorine was used. The last column in Table V gives the cost of treatment per million gallons, calculated on the cost of alum at $1.50 per 100 lbs. and wash water at 3 cents per 1000 gal. Since the Treasury standards can be met, it is more economical to run the plant at a lower efficiency with less alum and more wash water. This probably would not be true if the raw water were more polluted.

The data in Table V represent averages of daily results taken during the six months prior to cleaning the sedimentation basin in February. During this time the period of sedimentation was about 4 hrs. Table VI contains similar data on the operation after the sedimentation basin was cleaned, and the period of retention was 6 hrs. These data begin with an alum treatment of 0.21 gr. per gal. and extend through 0.95 gr. per gal. Further collection of data has been stopped because of air troubles in the filters which make comparison of filter runs impossible. The data in Table VI lead us to approximately the same conclusion as that in Table V.

The constancy of the composition of the Highland Park water has made it possible for these preliminary experiments which could not have been accomplished on a river plant. The operation confirms the data in Series I on a water with constant alkalinity and variable turbidity. Confirmation of the data in Series II and III must be left to the plant handling a water with a variable alkalinity. Data on a plant using lime or soda ash would be most interesting and valuable. The subject of color removal has not been studied because the Highland Park supply does not contain color.

CONCLUSION

1—Gillespie's method for determination of pH values without the use of buffer solutions is recommended for the average waterworks laboratory.

2—Laboratory tests indicate that the amount of alum required for the coagulation of a water is dependent on the alkalinity (the buffer value of the water) and independent of turbidity.

3—Coagulation begins at a pH of 7.8, and is fairly good at 7.6 in the summer months. These values are a little lower in the winter.

4—The pH zone in which the floc is well coagulated and settles readily, lies between 7.6 and 6.6.

5—Most efficient results are obtained at the Highland Park plant when the pH of the treated water is from 7.2 to 7.3.

6—Because of the relatively good water to start with, it is more economical to run the plant at a lower efficiency with less alum and more wash water than would be used at a pH of 7.2 to 7.3.

The Preparation of Phenylglycine-*o*-carboxylic Acid[1,2,3]

I—From Anthranilic Acid and Chloroacetic Acid

By Herbert L. Haller

Color Laboratory, Bureau of Chemistry, Washington, D. C.

The following paper is a record of the study of the reaction between anthranilic acid and chloroacetic acid for the preparation of phenylglycine-o-carboxylic acid.

The proper concentration in water of the reacting substances, time of reaction, ratio of anthranilic acid to chloroacetic acid, condensing agent, and temperature have been determined.

The best yields of phenylglycine-o-carboxylic acid were obtained when the following conditions were observed:

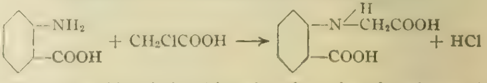
Concentration: [illegible] of anthranilic acid in 200 cc. of water.
Ratio: 2 mols of anthranilic acid to 1 mol of chloroacetic acid.
Condensing agent: [illegible] mols of sodium carbonate to 1 mol of chloroacetic acid.
Temperature: 90° C.
Time: 1 hr.

The use of an alkali carbonate as a condensing agent gives a better yield of phenylglycine-o-carboxylic acid than an equivalent amount of an alkali hydroxide.

IN A RECENT paper[4] from this laboratory the various steps involved in the so-called Heumann process for the production of indigo from naphthalene are given and the statement is made that a study of the different reactions involved in this process has been undertaken. This paper deals with the preparation of phenylglycine-*o*-carboxylic acid from anthranilic acid by condensing it with chloroacetic acid.

Two methods for preparing phenylglycine-*o*-carboxylic acid[5] are in general use:

1—Anthranilic acid is condensed with chloroacetic acid:



2—Anthranilic acid is subjected to the action of a mixture of formaldehyde and potassium cyanide:

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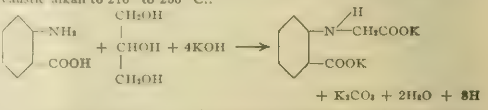
[1] Presented before the Division of Dye Chemistry at the 63rd Meeting of the American Chemical Society, Birmingham, Ala., April 3 to 7, 1922.

[2] Published by permission of the Department of Agriculture.

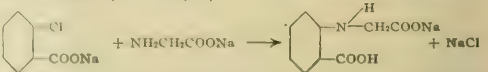
[3] Published as Contribution No. 63 from the Color Laboratory, Bureau of Chemistry, Washington, D. C.

[4] M. Phillips, J. Ind. Eng. Chem., 13 (1921), 759.

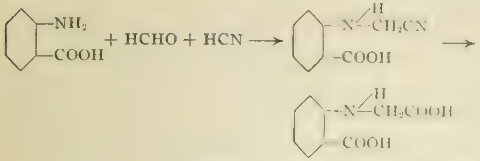
[5] According to D. R. P. 111,067 this compound is formed when anthranilic acid is heated with glycerol or other polyhydroxy compounds and caustic alkali to 210° to 250° C.:



It can also be obtained by heating *o*-chlorobenzoic acid with sodium glycine to about 220° C. (D. R. P. 12,546):



For the production of large quantities of indigo these starting materials are not abundant enough, besides being too expensive.



A study of the second method is planned and results will be published as soon as the experimental part has been completed. It is not known whether this method is more profitable than the alternative one using chloroacetic acid. However, it has recently been extensively used, especially during the war when methods[6] not requiring acetic acid became very important owing to the fact that supplies of acetic acid were requisitioned in all belligerent countries for the manufacture of munitions.

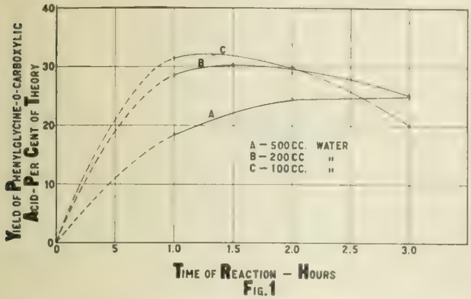


Fig. 1

Review of Literature

Phenylglycine-*o*-carboxylic acid was first prepared by Mauthner and Suida.[7] These investigators first attempted to prepare it from *o*-tolylglycocoll by oxidation, but were not successful. The fusion of anthranilic acid and chloroacetic acid also failed to produce phenylglycine-*o*-carboxylic acid. Even when the fusion temperature was held below the melting point of anthranilic acid, decomposition took place with evolution of carbon dioxide. Their best results were obtained by dissolving anthranilic acid, chloroacetic acid, and sodium carbonate in water and boiling the solution for several hours. After repeated experiments, a yield of 70 to 80 per cent was obtained. According to D. R. P. 127,178, considerable quantities of anthranilodiacetic acid are formed in this procedure.

The original Heumann patent[8] states that phenylglycine-*o*-carboxylic acid is obtained by heating monohalogenoacetic acid and anthranilic acid, with or without water, from 1 to 2 hrs. at about 100° C. or over. A longer time is required for the reaction at a lower temperature. In a later patent[9] it is stated that very little anthranilodiacetic acid is formed with this procedure but that some of the phenylglycine-*o*-carboxylic acid is decomposed, owing to the high temperature used in carrying out the reaction. The addition of sodium carbonate does not materially decrease the decomposition.

In the last-mentioned patent, decomposition of the phenylglycine-*o*-carboxylic acid is prevented by the use of neutral salts of anthranilic acid and chloroacetic acid. The reaction is carried out in not too dilute solutions at a temperature not exceeding 40° C. An acid salt of phenylglycine-*o*-carboxylic acid is formed, which is insoluble in the cold reaction mixture and can therefore readily be filtered off. The patent states that no anthranilodiacetic acid is formed in this procedure.

According to Levinstein,[10] the conversion of anthranilic acid to phenylglycine-*o*-carboxylic acid is effected at low temperatures by dissolving anthranilic acid in caustic soda, thoroughly cooling the solution, and adding the chloroacetic acid dissolved in water. The mixture is kept alkaline by further additions of caustic soda during prolonged stirring, after which it is partly dried, then "hydro" extracted, when the phenylglycine-*o*-carboxylic acid is obtained as the residue.

Experimental Procedure

To ascertain the most favorable conditions for the preparation of phenylglycine-*o*-carboxylic acid from anthranilic acid and chloroacetic acid, a study was made of the five following factors affecting the yield of phenylglycine-*o*-carboxylic acid:

(1) Concentration in water of the reacting substances.
(2) Time of reaction.[11]
(3) Ratio of the reacting materials.
(4) Condensing agent.
(5) Temperature of the reaction mixture.

Experiments were performed in which the concentration of the reacting substances was made the only variable, while the time of reaction, the ratio of anthranilic acid to chloroacetic acid, and the temperature of the reaction mixture were maintained constant. Another set of experiments was conducted in which the time of reaction was the only variable factor, while the concentration of the reacting substances, the ratio of anthranilic acid to chloroacetic acid, and the temperature remained constant. From the data obtained in this manner the best conditions were deduced for time of reaction and for concentration of the reacting substances. Experiments were then performed varying the ratio of reacting materials and employing the time and concentration found to be the most desirable. To substantiate the time of reaction factor, experiments were carried out for 1, 2, and 3 hrs. with variable ratio of anthranilic acid to chloroacetic acid and constant volume and temperature. Having thus determined the proper concentration of reacting materials, the time of reaction, and the ratio of anthranilic acid to chloroacetic acid, conducive to maximum yield of phenylglycine-*o*-carboxylic acid, calculated on the basis of anthranilic acid consumed, experiments were performed in which these factors were kept constant while varying quantities of a condensing agent were added. By thus repeating the procedure outlined above it was possible to obtain data on all the factors affecting the yield of phenylglycine-*o*-carboxylic acid.

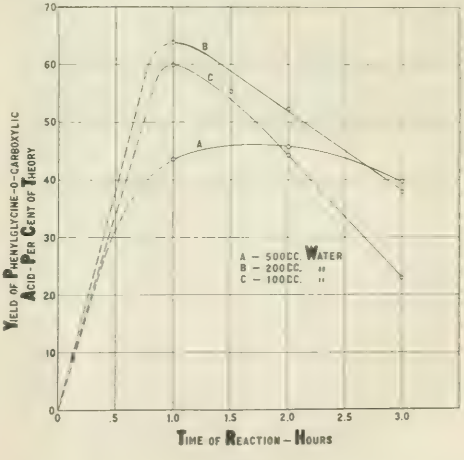


Fig. 1a

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[6] Georgievics and Grandmougin, "A Text-Book of Dye Chemistry," 2nd English ed., **1920**, 409.

[7] *Monatsh.*, **9** (1888), 727.

[8] D. R. P. 56,273.

[9] D. R. P. 127,178; U. S. Patent 690,325.

[10] *J. Soc. Dyers Colour.*, **17** (1901), 140.

[11] As used throughout this paper, this term refers to the time during which the reactions were permitted to proceed.

METHOD—Twenty-five grams of anthranilic acid in a 1-liter, short-neck, round-bottom flask were covered with 50 cc. less than the total volume of water employed in the experiment, and mixed as effectively as possible by shaking the flask.[12] To this was added the calculated amount of chloroacetic acid[13] dissolved in 50 cc. of water. The flask was heated under a reflux condenser in an oil bath to the desired temperature, the mixture being stirred by a mercury-sealed mechanical stirrer. Two thermometers, placed in the oil bath and in the reaction mixture, respectively, recorded the temperature. Stirring was continued throughout the reaction. Upon completion of the time of reaction, the oil bath was removed, the stirring continued, and after about 10 to 15 min.[14] the solution was acidified with hydrochloric acid. After standing 24 hrs. the precipitate which had formed was filtered off and washed with water, keeping the washings separate from the mother liquor. The precipitate was dried at 100° C. and weighed. Sodium acetate (70 g.) was dissolved in the mother liquor by stirring. After standing over night the precipitated anthranilic acid was filtered off, washed once or twice with water and dried at 100° C. This was pure anthranilic acid,[15] m. p. 143° to 144° C. To the filtrate and washings about 10 g. of sodium acetate and excess saturated copper acetate solution were added. After standing for 5 to 6 hrs. the precipitated copper anthranilate was filtered off, washed once or twice with water, and dried at 100° C.

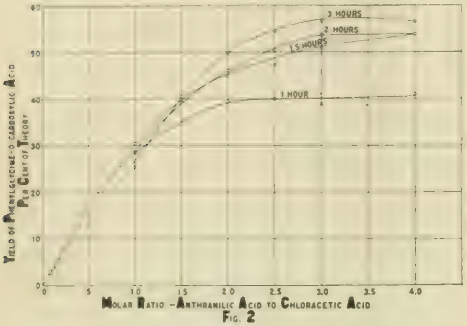

FIG. 2

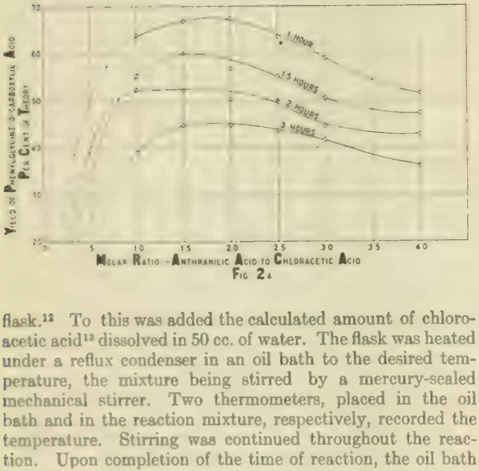

FIG 2A

MATERIALS—The anthranilic acid used was a product known as "Anthranilic Acid, Refined." It melted at 143° to 144° C., and analyzed 10.10 per cent N (calcd. for $C_7H_7O_2N$, N = 10.22 per cent). The chloroacetic acid was a good grade and analyzed 36.9 per cent Cl (calcd. for $C_2H_3O_2Cl$, Cl = 37.52 per cent). The other chemicals were all of C. P. grade and analyzed as follows: Sodium carbonate, 99.5 per cent Na_2CO_3; potassium carbonate, 86 per cent K_2CO_3; sodium hydroxide, 99 per cent NaOH; potassium hydroxide, 88.3 per cent KOH. The sodium hydroxide and the potassium hydroxide were of an unusually high degree of purity.

DETERMINATION OF PURITY OF PHENYLGLYCINE-o-CARBOXYLIC ACID—The purity of the reaction product was determined by obtaining its melting point, determining the nitrogen content by the Kjeldahl method, and titrating against standard alkali.

EFFECT OF VARYING TIME OF REACTION AND CONCENTRATION OF THE REACTING SUBSTANCES

The effect of varying the time of reaction and the concentration of the reacting substances, while the temperature (b. p. of reaction mixture is 100° + C.) of the reaction mixture and the ratio of anthranilic acid to chloroacetic acid (1 mole: 1 mole) remained constant, is indicated in Table I and graphically shown in Fig. 1. In Fig. 1A are given the results obtained when the yield of phenylglycine-o-carboxylic acid is based on the anthranilic acid consumed in the experiment. The consumed anthranilic acid is computed as the difference between the anthranilic acid originally taken and that recovered from the mother liquor.

TABLE I—EFFECT OF VARYING TIME OF REACTION AND CONCENTRATION OF REACTING SUBSTANCES

Ratio of $C_6H_4NH_2COOH.CH_2ClCOOH = 1:1$ (25 g.:17.2 g.)
Temperature = Boiling point of reaction mixture (100°+ C.)

				Yield of Phenylglycine-o-carboxylic Acid		
Expt. No.	Time of Reaction Hrs.	Water Cc.	Anthranilic Acid Consumed Grams	Grams	Per cent Theory	Based on Anthranilic Acid Consumed, Per cent Theory
1	1	500	15.4	6.42	18.1	43.6
2	2	500	13.3	8.67	24.4	45.9
3	3	500	15.7	8.91	25.0	39.8
4	1	200	16.2	10.17[1]	28.6	63.9
5	1.5	200	13.7	10.80	30.4	55.3
6	2	200	13.9	10.30	29.0	52.3
7	3	200	19.9	9.00	25.3	39.0
8	1	100	13.2	11.20[2]	31.5	60.0
9	2	100	17.5	10.63	29.9	42.5
10	3	100	21.8	7.14	20.0	23.0

[1] M. p. 207° C.; found 7.04 per cent N; calcd. for $C_9H_9O_4N$, N = 7.18 per cent.

[2] M. p. 206° C.; found 7.08 per cent N; calcd. for $C_9H_9O_4N$, N = 7.18 per cent.

The foregoing results indicate that the maximum yield of phenylglycine-o-carboxylic acid, based on the anthranilic acid consumed, is obtained when the time of reaction is 1 hr. and the concentration of the solution is 25 g. of anthranilic acid and 17.2 g. of chloroacetic acid in 200 cc. of water. It seems that at a higher concentration, while the reaction between anthranilic acid and chloroacetic acid takes place more rapidly, more of the anthranilic acid is destroyed. In the following experiments, therefore, the time of reaction was 1 hr. and the concentration of the solution 25 g. of anthranilic acid in 200 cc. of water.

EFFECT OF VARYING RATIO OF ANTHRANILIC ACID TO CHLOROACETIC ACID

The results of several experiments varying the ratio of anthranilic acid to chloroacetic acid while the other factors remained constant are given in Table II and shown graphically in Figs. 2 and 2A. The data for Fig. 2 are based on the anthranilic acid consumed in the experiment. To substantiate the time of reaction factor, experiments were also conducted, with a variable ratio of anthranilic acid to chloroacetic acid, for different periods of time. The results are recorded in Table II and in Figs. 2 and 2A.

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[12] When a [illegible] was employed, it was added at this point.

[13] The [illegible] was prepared by dissolving 86.1 g. of chloroacetic acid in 250 cc. of water [illegible] part of [illegible] was diluted to 50 cc.

[14] When a [illegible] employed, it is advantageous to cool the reaction mixture thoroughly before acidifying.

[15] Eighty per cent of the unchanged anthranilic acid can be recovered in this way.

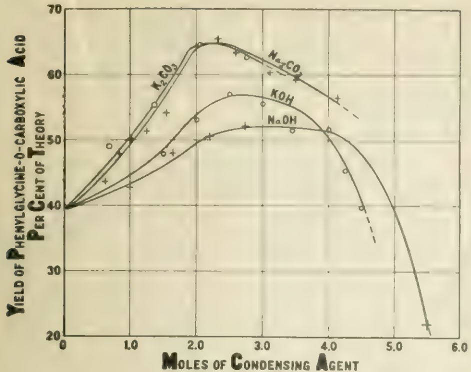

Fig. 3

Table II—Effect of Varying Ratio of Anthranilic Acid to Chloroacetic Acid with Variable Time of Reaction

25 g. anthranilic acid used in each experiment
25 g. anthranilic acid (1 mol) : 17.2 g. chloroacetic acid (1 mol)
Water = 200 cc.

Temperature = Boiling point of reaction mixture (100°+ C.)

Expt. No.	Molecular Ratio: Anthranilic Acid to Chloroacetic Acid	Chloroacetic Acid Used Grams	Time of Reaction Hrs.	Anthranilic Acid Consumed Grams	Yield of Phenylglycine-o-carboxylic Acid: Grams	Per cent Theory	Based on Anthranilic Acid Consumed, Per cent Theory
1	1.0	17.2	1	11.2	10.17	28.6	63.9
2	1.33	12.9	1	9.5	8.90	33.4	66.0
3	1.5	11.5	1	8.7	8.26[1]	34.8	66.8
4	2.0	8.6	1	6.8	6.80[2]	39.4	67.4
5	2.5	6.9	1	6.3	5.70	40.0	63.6
6	3.0	5.7	1	5.5	4.60	38.8	59.0
7	4.0	4.3	1	5.0	3.65	41.0	51.5
8	1.0	17.2	1.5	13.7	10.80	30.4	55.3
9	1.5	11.5	1.5	11.3	9.42	39.8	58.0
10	2.0	8.6	1.5	10.3	8.00	45.0	54.8
11	2.5	6.9	1.5	8.9	6.72	47.2	53.2
12	3.0	5.7	1.5	8.4	6.03	51.0	50.6
13	4.0	4.3	1.5	7.1	4.82	54.0	47.3
14	1.0	17.2	2	13.8	10.30	29.0	52.3
15	1.5	11.5	2	12.9	9.60	40.5	52.2
16	2.0	8.6	2	11.5	8.20	46.1	50.2
17	2.5	6.9	2	10.2	7.20	50.6	50.0
18	3.0	5.7	2	10.0	6.35	53.7	44.6
19	4.0	4.3	2	7.9	4.80	53.9	42.8
20	1.0	17.2	3	16.2	9.00	25.3	39.0
21	1.5	11.5	3	14.6	9.30	39.3	44.7
22	2.0	8.6	3	13.9	8.86	49.8	44.8
23	2.5	6.9	3	12.5	7.77	54.6	43.7
24	3.0	5.7	3	11.4	6.73	56.8	41.7
25	4.0	4.3	3	9.7	4.95	55.7	36.0

[1] M. p. 206° to 7° C.; found 7.17 per cent N; calcd. for $C_9H_9O_4N$, N = 7.18 per cent.

[2] M. p. 206° to 7° C.; found 7.00 per cent N; calcd. for $C_9H_9O_4N$, N = 7.18 per cent.

The results show that the maximum yield of phenylglycine-*o*-carboxylic acid is obtained when a ratio of 1.5 to 2.0 mols of anthranilic acid to 1 mol of chloroacetic acid is used. The actual yield of phenylglycine-*o*-carboxylic acid is somewhat better when the molecular ratio of anthranilic acid to chloroacetic acid is 2 to 1. In the subsequent experiments, therefore, a ratio of 2 mols of anthranilic acid to 1 mol of chloroacetic acid was maintained.

Effect of Adding a Condensing Agent

Using the above-determined optimum conditions for concentration of anthranilic acid, time, ratio of anthranilic acid to chloroacetic acid, and with the temperature at the boiling point of the reaction mixture, experiments were performed to determine the effect of adding varying amounts of a condensing agent. Sodium and potassium carbonates and hydroxides were used. The results of several experiments are given in Table III and graphically shown in Figs. 3 and 3A. In Fig. 3A results are based on the anthranilic acid consumed in the experiment.

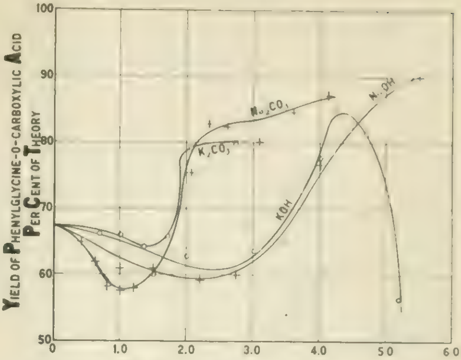

Fig. 3A

Table III—Effect of Adding a Condensing Agent

Ratio of $C_6H_4NH_2COOH : CH_2ClCOOH = 2 : 1$ (25 g. : 8.6),
Water = 200 cc. Time of reaction = 1 hr.
Temperature = Boiling point of reaction mixture (100°+ C.)

Expt. No.	Condensing Agent: Grams	Molar Ratio Condensing Agent to Chloroacetic Acid	Anthranilic Acid Consumed Grams	Yield of Phenylglycine-o-carboxylic Acid: Grams	Per cent Theory	Based on Anthranilic Acid Consumed, Per cent Theory
	Sodium Carbonate					
1	0	0	6.8	6.80	39.4	67.4
2	2.0	0.21	8.9	7.95	44.7	63.0
3	4.0	0.41	8.5	7.86	44.2	65.0
4	6.0	0.62	8.8	7.75	43.6	62.0
5	8.0	0.83	10.4	8.55	48.0	58.2
6	10.0	1.04	10.9	8.93	50.2	57.6
7	12.0	1.24	16.1	9.15	51.4	58.0
8	15.0	1.55	16.0	9.62	54.1	61.3
9	20.0	2.07	10.7	11.48[1]	64.4	75.5
10	22.5	2.33	9.9	11.65[2]	65.5	82.8
11	25.0	2.59	9.6	11.26	63.3	82.5
12	30.0	3.10	9.4	10.71	60.2	80.2
13	35.0	3.62	8.8	10.58	59.4	84.7
14	40.0	4.14	8.1	10.05	56.5	87.3
	Potassium Carbonate					
15	10.0	0.68	9.2	8.70	49.0	67.1
16	20.0	1.37	10.8	9.83	55.3	64.2
17	25.0	1.71	10.9	10.17	57.2	65.8
18	30.0	2.05	10.2	11.43[3]	64.3	79.2
19	40.0	2.73	9.8	11.10	62.4	79.8
	Sodium Hydroxide					
20	3.65	1.00	8.7	7.58	42.7	61.2
21	4.0	1.10	8.7	8.34	46.9	67.5
22	6.0	1.65	9.5	8.53	48.0	63.2
23	8.0	2.20	10.7	9.00	50.6	59.2
24	10.0	2.74	10.9	9.27	52.1	60.0
25	14.6	4.00	8.4	9.17[4]	51.5	76.7
26	20.0	5.48	3.1	3.96	22.1	90.5
27	30.0	8.22	4.5	1.03	5.7	22.6
	Potassium Hydroxide					
28	5.78	1.00	9.1	8.58	48.2	66.0
29	8.67	1.50	10.0	8.50	47.8	60.1
30	10.00	1.73	9.9	8.52	47.9	60.7
31	11.56	2.00	10.5	9.42	53.0	62.8
32	14.45	2.50	10.6	10.15	57.0	67.4
33	17.35	3.00	10.4	9.87	55.5	63.7
34	20.00	3.45	9.8	9.14	51.4	65.3
35	23.12	4.00	8.3	9.15[5]	51.4	77.7
36	24.57	4.25	6.7	8.10	45.5	85.2
37	26.01	4.50	6.1	7.07	39.7	81.4
38	30.00	5.19	1.9	1.52	8.6	56.3

[1] M. p. 206° to 7° C.; found 7.18 per cent N; calcd. for $C_9H_9O_4N$, N = 7.18 per cent.

[2] M. p. 206° to 7° C.

[3] M. p. 205° to 6° C.

[4] M. p. 206° to 7° C.

[5] M. p. 204° to 5° C.

It appears that when one of the alkali carbonates is employed as a condensing agent, a better yield of phenylglycine-*o*-carboxylic acid is obtained than with an equivalent amount of one of the alkali hydroxides. This probably is caused by the much less rapid hydrolysis of the chloroacetic acid by the carbonates. Since potassium carbonate and sodium carbonate yield approximately the same results, the cheaper sodium carbonate is naturally to be preferred. On the basis of the anthranilic acid consumed (Fig. 3A) it appears that 4 mols of sodium carbonate give the maximum yield of phenylglycine-*o*-carboxylic acid. Fig. 3, however, shows that the maximum actual yield of acid is obtained when slightly more than 2 mols of sodium carbonate is employed, and that the formation of phenylglycine-*o*-carboxylic acid rapidly decreases as the amount of sodium carbonate is increased. In the following experiments, therefore, 2.33 mols (22.5 g.) of sodium carbonate were employed.

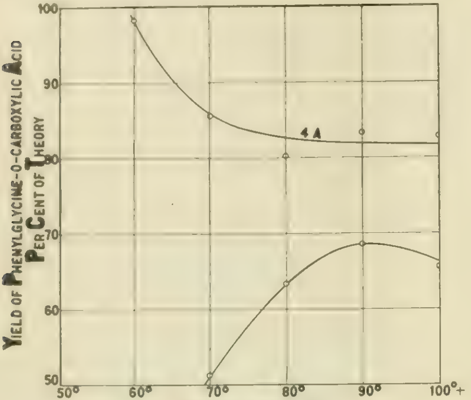

Fig. 4

Effect of Varying Temperature

Having determined the proper concentration of anthranilic acid, time of reaction, ratio of anthranilic acid to chloroacetic acid, and condensing agent, experiments were performed at different temperatures. The results of several experiments are given in Table IV and Fig. 4. Curve 4A gives the results when the yields are based on the anthranilic acid consumed in the experiment.

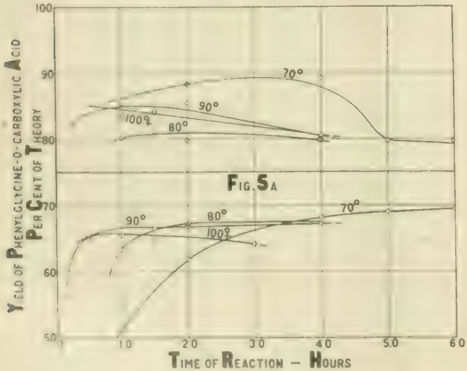

Fig. 5

At temperatures somewhat below the boiling point of the reaction mixture the reaction proceeds rather slowly and therefore it was thought desirable to conduct experiments for different periods of time at these lower temperatures. In order to substantiate the time of reaction factor, experiments were also conducted for different periods of time at 90° C. and at the boiling point of the reaction mixture. The results of several experiments are given in Table V and graphically shown in Figs. 5 and 5A. In the latter figure results are computed on the basis of the anthranilic acid consumed in the experiment.

Table IV—Effect of Varying the Temperature of the Reaction Mixture

Ratio of $C_6H_4NH_2COOH \cdot CH_2ClCOOH = 2:1$ (25 g.: 8.6 g.)
Water = 200 cc. Time of reaction = 1 hour
Condensing agent = 22.5 g. Na_2CO_3

			Yield of Phenylglycine-o-carboxylic Acid		
Expt. No.	Temperature °C.	Anthranilic Acid Consumed Grams	Grams	Per cent Theory	Based on Anthranilic Acid Consumed, Per cent Theory
1	25	0	0	0	0
2	40	0	0	0	0
3	60	3.8	5.3	29.8	98.2
4	70	7.5	9.1	51.2	85.5
5	80	9.9	11.26[1]	63.3	80.2
6	90	10.3	12.2[2]	68.6	83.3
7	100+	9.9	11.65[3]	65.5	82.8

[1] M. p. 206° to 7° C.
[2] M. p. 207° C.
[3] M. p. 206° to 7° C.

Table V—Effect of Varying Time of Reaction with Variable Temperature

Ratio of $C_6H_4NH_2COOH:CH_2ClCOOH = 2:1$ (25 g.: 8.6 g.)
Na_2CO_3 = 22.5 g. Water = 200 cc.

				Yield of Phenylglycine-o-carboxylic Acid		
Expt. No.	Time Hrs.	Temperature °C.	Anthranilic Acid Consumed Grams	Grams	Per cent Theory	Based on Anthranilic Acid Consumed, Per cent Theory
1	1	70	7.5	9.10	51.2	85.5
2	2	70	8.7	11.00	61.8	88.3
3	4	70	9.6	12.17[1]	68.3	89.3
4	5	70	10.8	12.27[2]	69.0	79.3
5	6	70	10.9	12.38	69.5	79.8
6	1	80	9.9	11.26[3]	63.3	80.2
7	1.5	80	10.5	12.12[4]	68.1	81.2
8	2	80	10.5	11.94	67.2	79 8
9	4	80	10.5	11.92	67.2	79.8
10	0.25	90	9.4	10.93	61.5	82.0
11	0.5	90	9.5	11.55[5]	65.0	85.4
12	1	90	10.3	12.20[6]	68.6	83.3
13	1.5	90	9.9	11.82	66.5	84.0
14	2	90	9.8	11.90	66.9	85.5
15	4	90	10.5	11.97	67.3	80.0
16	0.5	100+	9.6	11.60[7]	65.3	85.0
17	1	100+	9.9	11.65[8]	65.5	82.8
18	1.5	100+	9.6	11.50	64.7	84.3
19	2	100+	10.0	11.92	67.0	83.8
20	4	100+	10.0	11.41	64.2	80.6

[1] M. p. 205° to 6° C.
[2] M. p. 203° C.
[3] M. p. 206° to 7° C.
[4] M. p. 206° C.
[5] M. p. 205.5° to 6.5° C.
[6] M. p. 207° C.
[7] M. p. 206° to 7° C.
[8] M. p. 206° to 7° C.

The results indicate that the maximum yield of phenylglycine-*o*-carboxylic acid is obtained when the reaction is conducted at 90° C. for 1 hr. This substantiates the results obtained for the time of reaction factor in the previous experiments. Approximately identical results are obtained when the reaction is conducted at 70° C. for 4 hrs. At lower temperatures the reaction proceeds too slowly to be of any practical significance.

Educational programs of the various institutions offering courses in chemical engineering are to be investigated by a committee of eleven appointed by the council of the American Institute of Chemical Engineers, with a view to standardizing the training required for the degree of Ch.E. The program of the committee contemplates three years' work in obtaining the adoption of recommendations of a previous committee and the publication of a list of approved schools at the end of this period. The committee consists of H. C. Parmalee, *chairman;* five representative educators: Joseph H. James, W. K. Lewis, A. H. White, R. H. McKee, and S. W. Parr; and five representative industrialists: C. E. K. Mees, A. D. Little, C. L. Reese, W. C. Geer, and W. R. Whitney.

An erroneous report has been circulated regarding a fire which started on the premises of A. Daigger & Co., Chicago. The fire occurred in the block in which this company is located, but no damage was done to property of the Daigger Company.

Determination of Total Nitrogen in Cyanamide and Nitrate Mixtures—Davisson-Parsons Method[1,2]

By Kenneth D. Jacob and Walter J. Geldard

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A comparison has been made of the generally accepted methods for the determination of total nitrogen in fertilizer mixtures with the Davisson-Parsons method on mixtures containing cyanamide and nitrate nitrogen.

The usual methods do not give accurate results on mixtures containing considerable moisture. The Davisson-Parsons method, on the other hand, gives accurate results not only on solid mixtures but also on aqueous solutions.

IN CONNECTION with an investigation on commercial calcium cyanamide (hereafter referred to as cyanamide), it became necessary to determine the total nitrogen in mixtures of cyanamide and nitrates. Several methods for the determination of total nitrogen, including nitrate nitrogen, in fertilizer mixtures have been adopted as "Official" by the Association of Official Agricultural Chemists. It is, however, well known that these methods do not give accurate results in the presence of much moisture. Mixtures of cyanamide and calcium nitrate usually contain considerable moisture, and in preliminary experiments we found that consistent results for total nitrogen could not be obtained by any of the official methods. A method for the determination of total nitrogen, including nitrate nitrogen, perfected by Davisson and Parsons[3] for the analysis of soil and biological extracts, seemed to offer possibilities in this connection. In making a study of the applicability of this method to mixtures such as here considered, two official methods were also studied in comparison. These were the Gunning-Forster method, as used by the Nitrogen Laboratory of the Bureau of Chemistry, and the Gunning method modified to include the nitrogen of nitrates, and were selected as probably being the most reliable of the official methods for the determination of total nitrogen in cyanamide-nitrate mixtures.

Outline of Methods

To avoid any confusion that might arise from referring to the various methods by name only, they are briefly described as follows:

The Gunning-Forster Method—To the weighed sample add 35 cc. of concentrated sulfuric acid (sp. gr. 1.84) containing 33.33 g. salicylic acid per liter. Mix thoroughly and let stand over night. Add 5 g. sodium thiosulfate, let stand for 4 hrs., and then digest for about 10 min., beginning with a low flame and increasing to vigorous boiling as foaming subsides. Cool, add 10 g. potassium sulfate, and boil steadily for at least 3 hrs. Cool, dilute, and distil in the usual way.

This method is known to give accurate results when the sample is finely powdered and dry. It is especially important that the sample be dry, for as little as 4 per cent of moisture will cause low results.

The Gunning Method, Modified to Include the Nitrogen of Nitrates[4]—This method is practically the same as the Gunning-Forster, with the exception that the sample is left in contact with the sulfuric-salicylic acid mixture, with frequent shaking, for only 30 min. The sodium thiosulfate is then added and allowed to stand about 10 min. before proceeding with the digestion.

It is open to the same objection as the Gunning-Forster method. The effect of moisture in samples has already been pointed out by several investigators[3,5] and our results further confirm their conclusions.

The Davisson-Parsons Method—The sample is placed in an 800-cc. Kjeldahl flask, 100 to 200 cc. distilled water added with sufficient 50 per cent sodium hydroxide to make the solution tenth normal. Sufficient Devarda's alloy (Cu—50, Al—45, Zn—5) to reduce all the nitrate nitrogen is then added. (One gram of alloy will reduce about 25 mg. nitrate nitrogen.) The flask is then connected to a Davisson-Parsons absorption tube containing 35 cc. of sulfuric acid (4 : 1), and reduction of the nitrate nitrogen to ammonia carried out, after which the acid in the absorption tube is allowed to suck back into the flask, and the tube thoroughly washed with distilled water. The solution is then evaporated to charring, 5 to 7 g. potassium sulfate are added, and the digestion continued for about 1 hr. after the melt has become clear. The melt is then cooled, diluted, and distilled.

Since the determinations by this method were carried out exactly as recommended by Davisson and Parsons, the reader is referred to the original article for the exact details of procedure. The most important feature of this method is that the analysis is carried out in aqueous solution, and it is therefore immaterial whether the sample is solid or in solution. This eliminates the necessity of having the sample for analysis dry as in the case of the official methods.

A number of investigations[6] on the use of Devarda's alloy for the determination of total nitrogen in mixtures of nitric and organic nitrogen have been carried out within the past few years. After comparison with the other methods, the various investigators are almost unanimous in the opinion that more uniform and reliable results can be obtained under a wider variety of conditions by the use of Devarda's alloy than with any of the other proposed methods. The majority of the workers used either the Davisson-Parsons procedure directly or a slight modification of it.

Comparison of the Davisson-Parsons Method with Official Gunning Method for Cyanamide Nitrogen Alone

Before making comparative tests of the foregoing methods for total nitrogen, it was necessary to determine the accuracy of the Davisson-Parsons method on extracts of cyanamide. As to its use for nitrate nitrogen alone, the results of other investigators[7] are sufficient to indicate its accuracy.

A cyanamide extract was prepared by shaking a sample with water for 3 hrs., filtering, and making up to a definite volume. Aliquots of 50 cc. of this solution were analyzed

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[1] Received August 28, 1922.

[2] Published by permission of the Department of Agriculture.

[3] This Journal, **11** (1919), 306.

[4] "Methods of Analysis, A. O. A. C.," **1919**, p. 8.

[5] Peck, This Journal, **3** (1911), 817.

[6] Pilz, *Z. landw. Versuchw.*, **22** (1919), 180; Platou, *Chimie et industrie*, **3** (1920), 310; Flycht, *Caliche*, **1** (1919), 210; Baldi, *Giorn. chim. ind. applicata*, **2** (1920), 376; McLachlan, *Pharm. J.*, **106** (1921), 477; Strowd, *Soil Sci.*, **10** (1920), 333.

[7] Mitscherlich and Herz, *Landw. Jahrb.*, **38** (1909), 279; Davisson and Parsons, see Note 3; Butt, This Journal, **12** (1920), 352.

by the official Gunning[9] and Davisson-Parsons methods. The Gunning method (using potassium and copper sulfates) is recommended generally for total nitrogen in cyanamide and other fertilizer materials in the absence of nitrates.

The results of these analyses are given in the following table. All results given in this paper have been corrected for the nitrogen blank on the reagents alone.

TABLE I—COMPARISON OF THE OFFICIAL GUNNING AND DAVISSON-PARSONS METHODS ON THE DETERMINATION OF CYANAMIDE NITROGEN ALONE

MILLIGRAMS NITROGEN FOUND	
(A) Official Gunning	(B) Davisson-Parsons
29.11	29.12
29.06	29.20
29.03	29.12
29.10	29.08
Av. 29.07	Av. 29.13

These results indicate that the Davisson-Parsons method accurately determines the total nitrogen of cyanamide extracts. The total nitrogen value for a 50-cc. aliquot obtained in B, 29.13 mg., was used in the following as a basis for the cyanamide nitrogen contents in solutions containing both cyanamide and nitrate nitrogen.

COMPARISON OF METHODS ON MIXTURES CONTAINING BOTH CYANAMIDE AND NITRATE NITROGEN

AQUEOUS SAMPLES—The source of the nitrate nitrogen used in preparing these extracts was an approximately 0.04 *N* solution of nitric acid, carefully prepared from C. P. nitric acid. A series of nine analyses by the Davisson-Parsons method gave the average value for a 50-cc. aliquot of 28.57 mg. of nitrate nitrogen.

Using the two values as given above for cyanamide and nitrate nitrogen, a number of mixtures containing 50-cc. of each of the solutions were prepared and analyzed by the three methods previously outlined. The composition of the mixtures was as follows:

	Mg.
50 cc. cyanamide extract	29.13 nitrogen
50 cc. nitric acid solution...........	28.57
TOTAL	57.70

The analytical results obtained were as follows:

TABLE II—COMPARATIVE RESULTS ON AQUEOUS MIXTURES OF CYANAMIDE AND NITRATE NITROGEN

MILLIGRAMS NITROGEN FOUND		
Davisson-Parsons Method	Gunning-Forster Method[1]	Modified Gunning Method[1]
57.89	56.01	56.50
57.91	56.91	56.66
57.70	56.61	56.96
57.72	...	...
57.64	...	...
57.70	...	...
57.73	...	...
57.70	...	...
57.91	...	...
57.87	...	...
57.86	...	...
57.77	...	...
Av. 57.78	56.51	56.71

[1] As previously stated the Gunning-Forster and modified Gunning methods do not give reliable results in dilute solution; the 100-cc. samples were therefore evaporated very carefully to a volume of about 10 cc. before proceeding with the analyses. They could not be evaporated to dryness because of possible loss of nitrogen

These results indicate that the Davisson-Parsons method is applicable to solutions containing cyanamide and nitrate nitrogen. The results by this method agree closely and are as accurate as can usually be obtained in this type of determination. It should be noted that the effect of excess moisture is quite evident in the case of the official method, and for that reason only a limited number of determinations were made, as indicated in the above table.

SOLID SAMPLES LOW IN NITRATE NITROGEN—In analyzing solid samples of nitrates and cyanamide, the agreement between the methods is somewhat closer. For this test, a sample of cyanamide containing a known amount of calcium nitrate was prepared and analyzed by both the Gunning-Forster and Davisson-Parsons methods. The former method was selected rather than the modified Gunning because it is generally considered to give more accurate results. The composition of the sample was as follows:

	Per cent
Nitrate nitrogen	1.10
Cyanamide..................	15.53
TOTAL............	16.63

The analytical results are given in the following table:

TABLE III—COMPARISON OF METHODS ON SOLID MIXTURES OF CYANAMIDE AND NITRATE NITROGEN, LOW IN NITRATE NITROGEN

	Milligrams Nitrogen Found	Per cent Nitrogen
(A) Gunning-Forster Method	79.16	15.83
	81.49	16.29
	81.11	16.22
	79.85	15.97
AVERAGE.......	80.40	16.08
(B) Davisson-Parsons Method	83.34	16.67
	83.41	16.68
	83.43	16.69
AVERAGE.......	83.39	16.68

SOLID SAMPLES HIGH IN NITRATE NITROGEN—The mixture used above might be considered low in nitrate nitrogen, and therefore not a sufficient test of the reliability of the method. Another was prepared which contained more nearly equal parts of the two forms of nitrogen. Potassium nitrate (97.68 per cent) was mixed with cyanamide (20.42 per cent N) to produce a mixture of the following composition:

	Per cent
Nitrate nitrogen..............	7.73
Cyanamide nitrogen..........	8.78
TOTAL NITROGEN..........	16.51

The results of analyzing this mixture are given below:

TABLE IV—COMPARISON OF METHODS ON SOLID MIXTURES OF CYANAMIDE AND NITRATE NITROGEN, HIGH IN NITRATE NITROGEN

	Milligrams Nitrogen Found	Per cent Nitrogen
(A) Gunning-Forster Method	81.03	16.21
	79.37	15.87
	80.10	16.02
	79.47	15.89
AVERAGE.......	79.99	16.00
(B) Davisson-Parsons Method	83.02	16.60
	82.88	16.57
	83.02	16.60
	82.88	16.57
AVERAGE.......	82.95	16.58

Although neither of the two solid mixtures contained an appreciable quantity of free moisture, water was present combined as calcium hydroxide, since water is added to commercial cyanamide to hydrate the free lime. Moreover, cyanamide, when stored with access to the air, slowly absorbs additional moisture. Thus, it is readily seen that the cyanamide used in these mixtures might easily have contained a considerable quantity of combined water, which would be liberated on the addition of sulfuric acid, giving the low results noted above with the Gunning-Forster method.

In contrast to the unsatisfactory results given by other methods, those obtained with the Davisson-Parsons method are highly satisfactory and suggest the greater applicability of the method to fertilizers in general. Further work on this method with the view to its adoption as an official method for total nitrogen including nitrates therefore seems highly desirable.

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[9] "Methods of Analysis, A. O. A. C.," 1919, p.

Determination of the True Specific Gravity of Coke[1]

By Harold J. Rose

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Some of the methods in use for the determination of the true specific gravity of coke vary in important respects. This paper is presented to show the urgent need of an official method for this determination.

Data are given to show the effect of the degree of pulverization of the sample, the nature of the liquid used, the time of boiling and standing, and the effect of partial vacuum.

When 60-mesh coke samples were pulverized to pass a 200-mesh sieve, the true specific gravity was found to increase by as much as 12.7 per cent. The greatest increase was noted in the case of cokes which had been made below 800° C.

When the effect caused by a change of liquids was examined, benzene was found to give much the lowest results. Figures obtained by using benzene were as much as 8.1 per cent lower than those obtained by using water.

The true specific gravity of coke is usually determined for the purpose of calculating the porosity of the sample in question. The discrepancies mentioned above, when expressed in terms of porosity, amount to as much as 30 to 50 per cent of the total variation in porosity which will be found in different blast-furnace cokes.

Variations of the time of boiling and standing in the wetting liquid, and the use of partial vacuum during boiling, also produced discrepancies, although these were considerably smaller than those mentioned above.

THE TRUE specific gravity of coke is usually determined for the purpose of calculating its porosity. It is also of some value in judging the temperature at which the coke has been made. A number of methods for this determination have been published, but it appears that the problem is more complex than has been generally recognized.

According to methods published or in use, the determination may be made with pycnometer, volumeter, or by weighing coke pieces suspended from the beam of a balance. Some of these types of apparatus involve experimental errors and difficulties. The size of the particles of sample used in the different methods varies from a fine powder to full-sized coke pieces, and the exact fineness is not always specified. For the wetting liquid, water and organic liquids such as benzene, toluene, alcohol, and carbon bisulfide are variously used. Finally, boiling for long periods and the use of a partial vacuum may, or may not, be specified.

It was recently necessary in this laboratory to make a large number of determinations of the true specific gravity of coke with somewhat greater accuracy than that required for usual testing purposes. It was soon found that serious discrepancies were obtained when the kind of liquid was changed, or the degree of fineness of the sample was varied.

A survey of the scattered information available on the determination of the true specific gravity of coke soon indicated the desirability of making a brief compilation and comparison of a number of the methods that have been published or are in extended use. Unfortunately, space is not available for this résumé, and since methods in steel and coke plant use are for the most part unpublished, references cannot be given. It will be sufficient to state that such methods exist in considerable variety, and are in some cases obviously inaccurate.

Effect of Fineness of Sample

If the cellular nature of coke and its mode of formation be considered, it will be realized that a larger or smaller percentage of the total cell space may exist as small isolated cells. Unfortunately, this feature cannot be directly shown, as no comprehensive microscopic study of coke cell structure is available. Such cell spaces will not be penetrated by liquid in a true specific gravity determination, unless the cell walls have been broken by sufficiently fine grinding.

It is for this reason, presumably, that many methods require the use of finely powdered coke, the degree of fineness when specified ranging from 40 to 80 mesh. It has been found in this laboratory that a very distinct increase in the true specific gravity is obtained when the pulverization is carried to a still greater extent. No comparisons have been made with methods involving the use of large coke pieces, as this practice does not seem defensible from any standpoint.

Experimental Data on Influence of Fineness—Table I gives data concerning the effect of fineness of pulverization on the true specific gravity figure. The sample used consisted of a mixture of the middle thirds (the "cauliflower" and center of oven ends being rejected) of two full-sized pieces of by-product coke made from 100 per cent high volatile West Virginia coal.

The material was first crushed to 20-mesh size by means of steel rolls. 500 g. were then placed in an Abbé pebble mill—a porcelain jar 7 in. in inside diameter, and 7 in. deep, half filled with quartz pebbles. The pebble mill made 54 r. p. m. 100 g. portions were removed after the following intervals: 1 hr. 15 min., 2 hrs. 15 min., 5 hrs. 15 min. The remaining 200 g. were made into a thin paste with distilled water and were pebble-milled for another 24 hrs. Another sample was prepared by repeatedly passing a part of the original 20-mesh sample through steel rolls, and sieving. This process was continued until all had passed through a 60-mesh sieve.

A portion of each sample was dry-sieved in order to obtain an approximate idea of its fineness. Ash determinations were also made in duplicate, to find out whether or not mineral impurity was introduced during the prolonged grinding.

The determinations in Table I, and all others reported in this paper, were made in the following manner, except where otherwise noted.

Method Used—A 10-g. sample of coke which had been dried at 105° C. was introduced into a 50-cc. volumetric flask provided with a ground-glass stopper. The flask was filled about one-third full with C. P. benzene, and the mixture gently boiled on an electric hotplate for one-half hour. The flask was cooled, filled approximately to the mark with benzene, and placed for at least 15 min. in a water bath kept at exactly 25° C. The meniscus was adjusted to the mark at that temperature, and the flask was stoppered, wiped dry, and weighed.

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[1] Received March 28, 1922. Presented before the Division of Industrial and Engineering Chemistry at the 63rd Meeting of the American Chemical Society, Birmingham, Ala., April 3 to 7, 1922.

The calculations were made as follows:

Let S = weight of coke sample
B = weight of flask filled with benzene
D = weight of flask, coke, and benzene (after boiling).

Then

$$\text{True specific gravity} = \frac{S}{B + S - D} \times \text{sp. gr. benzene}$$

All results given in this paper have been calculated to true specific gravity at 25° C., referred to water at 15.5°. (15.5° C. is the usual coke plant standard and approximates 60° F.)

TABLE I

SAMPLE No.	METHOD OF PREPARATION	SIEVE TEST PER CENT		ASH CONTENT PER CENT		TRUE SPECIFIC GRAVITY
A-1	Steel-rolled	Through 60 mesh		7.01		1.699
		On 100 mesh	38.0			1.698
		On 200 mesh	34.8			
		Through 200 mesh	27.2			
					Av.	1.699[1]
A-2	Pebble-milled 1 hr. 15 min.	Through 60 mesh		7.06		1.678
		On 100 mesh	25.2			1.671
		On 200 mesh	46.8			
		Through 200 mesh	28.0			
					Av.	1.675
A-3	Pebble-milled 2 hrs. 15 min.	Through 60 mesh		7.10		1.710
		On 100 mesh	1.2			1.700
		On 200 mesh	34.8			
		Through 200 mesh	64.0			
					Av.	1.705
A-4	Pebble-milled 5 hrs. 15 min.	Through 200 mesh	100.0	7.09		1.739
						1.731
						1.734
					Av.	1.735
A-5	Pebble-milled 5 hrs. 15 min.	Through 200 mesh	100.0	9.02		1.753
						1.753
	dry, plus 24 hrs. wet				Av.	1.753

[1] A possible explanation of the fact that this value is higher than the succeeding one is that metallic iron may have been introduced during repeated passage through the steel rolls.

NOTE: Portions of the same sample of benzene were used throughout, and under identical conditions, so that the results above are strictly comparable.

COMMENTS ON TABLE I: (1) Since the wet-pebble milling of coke for 24 hrs. resulted in a 2 per cent increase in ash content, this treatment would not be permissible. The rise in the true specific gravity figure after wet grinding is 0.018. The calculated effect of the introduction of 1.93 per cent quartz happens to be exactly 0.018. Thus, in this instance, there appears to be no real gain in the true specific gravity when 200-mesh coke is pulverized still finer.

(2) Dry-pebble milling of a large sample for as long as 5 hrs. did not introduce more than a trace of mineral impurity.

(3) The maximum and minimum acceptable figures obtained above show a variation of 0.060, which amounts to 3.4 per cent.

From an examination of the results of other tests made at the same time, it was soon found that the effect of fineness of pulverization was still greater in the case of cokes made at comparatively low temperatures (below 800° C.). To secure information on this point, several series of cokes were made in the laboratory at various temperatures. In making these cokes a standard practice was followed, which proved to yield coke most nearly comparable to that obtained in full-scale operation.

The cokes obtained were crushed to 20-mesh size and divided into two portions. One portion was crushed in a diamond steel mortar to just pass 60 mesh. The other half was pulverized for about 3 hrs. in an Abbé pebble mill, until it readily passed through a 200-mesh screen.

Table II gives the results of tests on these cokes. The determinations were carried out in the same way as described for Table I.

TABLE II

SAMPLE No.	DESCRIPTION	Temp. of Coking ° C.	True Sp. Gr. of Coke 60 Mesh	True Sp. Gr. of Coke 200 Mesh	Increase of Sp. Gr. Due to Pulverization
B	[illegible] made	700	1.588	1.702	0.114
	[illegible]	750	1.633	1.798	0.165
	Pittsburgh Seam, high	850	1.742	1.817	0.075
	volatile coal	950	...	1.823	
C	[illegible]	700	1.639	1.723	0.084
	that when made the	750	1.693	1.800	0.107
	heating was continued	850	1.815	1.863	0.048
	for 2 hrs. [illegible]	[illegible]	1.842	1.886	0.044
D	Laboratory [illegible]	[illegible]	[illegible]	1.743	0.196
	from a [illegible]	[illegible]	[illegible]	1.735	0.058
	per cent [illegible]	[illegible]	1.840	1.846	0.006
	[illegible]				
	per cent low volatile material				

COMMENTS ON TABLE II: (1) The effect of fineness of pulverization is greatest in the case of cokes made in the laboratory at 700° and 750° C., the discrepancies at these temperatures averaging 8.6 per cent, and reaching a maximum of 12.7 per cent.

(2) When calculated to porosity

$$\left(\text{Porosity} = 100 - \frac{100 \times \text{apparent sp. gr.}}{\text{true sp. gr.}}\right)$$

assuming for convenience an apparent specific gravity of 0.900, these discrepancies average 4.5 per cent with a maximum of 6.6 per cent.

(3) Since the actual range of porosity of different blast furnace cokes is only about 15 per cent (from 42 to 57 when determined by a particular method), as small a matter as the degree of fineness of pulverization of a particular sample may make a difference 40 to 50 per cent as great as the variation to be expected between the densest and most porous cokes in use. It is clear that the degree of pulverization must be carefully regulated.

VARIATIONS DUE TO THE LIQUIDS USED

A series of determinations was made, using water, benzene, carbon tetrachloride, and carbon bisulfide. The organic liquids had been obtained from standard chemical supply houses, and were labeled "pure" or "C. P." The specific gravity of these liquids was determined by pycnometer, under the same conditions as were used for the tests with coke. Except for the variation in liquids used, the determinations of Table III were made according to the method immediately preceding Table I.

TABLE III

SAMPLE No.	TRUE SPECIFIC GRAVITY OF COKE Water	Benzene	Carbon Tetrachloride	Carbon Bisulfide
A-5 (See Table I)	1.838	1.750	1.851	1.865
	1.865	1.750	1.823	1.887
Average....	1.852	1.750	1.837	1.876

The low figure for true specific gravity obtained by using benzene will at once be noted. While the agreement between individuals of duplicate determinations is not especially good in some of these cases, the low results obtained with benzene are much too large to be ascribed to experimental error. The variation between results obtained by benzene and water in the instance above is 0.102. Several more determinations were made to further compare the results obtained by using benzene and water.

TABLE IV

SAMPLE No.	DESCRIPTION	TRUE SPECIFIC GRAVITY OF COKE Water	Benzene	Lowering of True Specific Gravity Due to Benzene
A-1	(See Table I)	1.870	1.699	
		1.828	1.698	
	Average......	1.849[1]	1.699	0.150
A-3	(See Table I)	1.876	1.753	
		1.869	1.753	
	Average......	1.873[1]	1.753	0.120
E	200 mesh sample "Cauliflower" $^{1}/_{3}$ of two pieces of coke made from 100 per cent high vol. W. Va. coal	1.922	1.809	
		1.901	1.804	
	Average......	1.912[1]	1.807	0.105
F	By-product coke from mixture of three Colorado coals	1.965	1.907	
		1.924	1.934	
	Average......	1.945	1.920	0.025

[1] These determinations were made by boiling for $2^{1}/_{2}$ hrs. under moderate vacuum.

The largest lowering of specific gravity due to the use of benzene that is recorded in Table IV, is 0.150, or 8.1 per cent.

When calculated to "porosity," as explained in the comments on Table II, this discrepancy will be about 30 per cent as great as the total variation in porosity of the most widely different blast-furnace cokes.

Variation Due to Prolonged Boiling and Standing

It was considered desirable to determine whether prolonged boiling or standing would increase the true specific gravity figure. The following determinations were made according to the method preceding Table I, except for the variation in the time of boiling and standing.

Table V

Sample No.	Description	True Specific Gravity of Coke (Time in Benzene)		
		1/2 Hr. Boiling	3 Hrs. Boiling	3 Hrs. Boiling and 16 Hrs. Standing in Cold
A-1	Through 60 mesh	1.699	1.711	1.714
	(See Table I)	1.698	1.706	1.709
	Average.......	1.699	1.709	1.712
A-4		1.731	1.755	1.748
	Through 200 mesh	1.739	1.755	1.748
	(See Table I)	1.734	...	1.741
	Average.......	1.735	1.755	1.746

It will be seen that the effect of prolonged boiling and standing is not large, the greatest discrepancy noted above being 0.020, and the average about half that.

Variation Due to Use of Vacuum

Since most methods which employ water specify the use of partial vacuum, it is of interest to know the importance of this detail, especially as the use of vacuum often introduces considerable experimental difficulty due to frothing. Only a single pair of determinations is available to illustrate this point.

Table VI

Sample No.		True Specific Gravity of Coke	
		1/2 Hr. Ordinary Boiling	2 1/2 Hrs. Boiling under Partial Vacuum
A-5	(See Table I)	1.838	1.880
		1.865	1.873
	Average.......	1.852	1.877

General Discussion of the Discrepancies

The purpose of this paper is to point out the necessity for the adoption of an official method for the determination of the true specific gravity of coke.

For important discussions as to the causes of large discrepancies in the determination of the density of charcoal, the reader is referred to the work of Cude and Hulett,[2] and to that of Harkins and Ewing.[3] These investigators have made an extensive study of the determination of the density of activated charcoal, using elaborate apparatus and extremely refined methods.

Cude and Hulett find that the liquid used, the fineness of pulverization of the sample, and the time of standing in contact with the liquid, all have an important effect on the result obtained. For example, the specific gravity of 18- to 20-mesh charcoal obtained by using carbon bisulfide was 0.337 higher than that obtained by using carbon tetrachloride. The values obtained when water and benzene were used were intermediate, benzene giving a figure 0.057 lower than that obtained by water. This last difference is of the same sign and of about the same magnitude as the writer has found when using coke.

The effect of fineness of pulverization as found by these investigators is shown by the following example: When a charcoal sample of 1.95 mm. grain size was pulverized to 0.001 mm. grain size, the specific gravity was found to increase by 0.137. Water was used as the wetting liquid. When 18- to 20-mesh charcoal was allowed to stand in water for 227 hrs., the specific gravity increased by 0.094.

The authors state: "As a first approximation we have considered the penetration to be proportional to the surface tension of the liquid and inversely proportional to its viscosity."

Harkins and Ewing investigated the use of eleven different liquids. They found, however, that in every case benzene gave a *higher* specific gravity than water, this difference in the three cases given being 0.165, 0.183, and 0.151. They suggest that their samples were more thoroughly outgassed than those of Cude and Hulett. Harkins and Ewing found that a given sample would absorb different volumes of different liquids, the volumes increasing with the compressibility of the liquid in question.

The writer has seen several comparisons of the use of benzene and water which have been made by coke plant laboratories. In general, these figures were too erratic to be of much value. They did, however, indicate that a consistent difference was not to be expected in results obtained by the two methods.

Suggested Official Method

The determination of the actual volume of coke substance present in a given sample may prove to be a difficult, or perhaps nearly impossible matter. If this should prove to be the case, an arbitrary choice will have to be made. For such an arbitrary choice, the writer suggests the use of water as a wetting liquid, the use of very finely pulverized coke (200 mesh), and a 30-min. boiling period. The use of vacuum may prove to be necessary, but the convenience of the method would be much increased if this feature could be omitted.

Water is recommended because it is readily obtainable in a pure condition and is noninflammable. Cude and Hulett consider water to have a greater penetrative power than benzene, and, according to this viewpoint, the specific gravity figure obtained by using water would be more nearly correct than the lower figure obtained by using benzene.

Acknowledgment

The writer wishes to express his appreciation of the assistance rendered by Miss H. E. Wassell and Miss G. E. Powley, who performed most of the specific gravity determinations reported in this paper.

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[2] *J. Am. Chem. Soc.*, **42** (1920), 391.

[3] *Ibid.*, **43** (1921), 1787.

Piracy

In discussing the purchase of apparatus in the editorial "Our Viewpoint," March 1922 issue, we called attention to the practice of some dealers who have come into the chemical field without experience with little responsibility and with the apparent purpose of making a profit on one order without regard to the future. There has now come to our notice a list of laboratory supplies, poorly mimeographed on both sides of the sheet and made up almost entirely from the catalogs of such reputable dealers as Eimer & Amend, Arthur H. Thomas, and Central Scientific Company. The list purports to be the catalog of the concern circulating it, and on the first page we find some queer bedfellows. The following is copied from the list:

25 Arsenic Apparatus Marsh's on wood support 276 E & A 145/1..	$1.75
25 Automatic Mauser (German) pistols brand new calibre 6.35 m/m (.25") new model 10 shot will fit American Ammunition......	14.00
25 Ditto 7.65 m/m (.32") 9 shot..................................	18.00
12 Balances, Hand scale, horn pan 10 cm. beam 454 E & A 392....	1.50
5 Ditto 15 cm. beam..	2.25

The layman finds many unusual things in a list of chemical apparatus, but never before have we found automatic German revolvers and ammunition listed with arsenic apparatus and balances. The large number of firearms with which bandits are supplied may have a foreign origin, and in any event we can offer no more striking example of unfair competition with established dealers than this instance.

Chemistry of Wood[1,2]

V—Results of Analysis of Some American Woods

By **G. J. Ritter**[3] and **L. C. Fleck**[4]

Forest Products Laboratory, Department of Agriculture, Madison, Wisconsin

The analyses of some American woods, as set forth in the following article, give the following results:

Hardwoods show a higher acetic acid content than softwoods by the acid hydrolysis process. Hardwoods average about 100 per cent higher in pentosan content than softwoods.

Softwoods have a higher methyl pentosan content than hardwoods. The methoxy content of softwoods is approximately 85 per cent of that found in hardwoods.

The cellulose isolated from the different species varies in furfural-producing substances. Softwood cellulose retains from 38 to 56 per cent of the furfural-yielding bodies in the original wood, and hardwood cellulose retains from 57 to 66 per cent of the furfural-yielding bodies.

Beta-cellulose content is higher in softwoods than in hardwoods.

Apparently the acetic acid content obtained by acid hydrolysis is lower than that obtained by destructive distillation.

The analyses of eight species of woods not previously determined are given.

American forests are rapidly becoming depleted of certain species of woods. The industries using these particular species are turning with increased interest to the use of other woods with similar physical and chemical properties. Where such similar essential characteristics occur in two or more woods, it is possible in many cases to substitute one for the other. In considering different woods for the same use, certain properties might be classified as primary and others as secondary. If the primary properties are satisfactory and the secondary are not, it may be possible by various treatments to render the woods suitable for the required purpose. This is strikingly illustrated in the paper industry, in which some woods are given the soda treatment, some the sulfate treatment, and still others the sulfite process treatment, in order to obtain pulp for paper.

If data were available on the chemical composition of more of the important American woods, it is believed that the wood-using industries could in some cases use woods in new processes, and in other instances utilize woods now considered of little value. With this in mind further work was done at the Forest Products Laboratory on the study of the chemical composition of some American woods, a project which was begun by A. W. Schorger[5] and continued by S. A. Mahood and D. E. Cable.[6]

In selecting the woods for this comparative analysis, an attempt was made to take some of the more useful woods which would confirm or disprove the general belief (1) that there is a relation between the density and the chemical composition of wood, and (2) that there is a relation between the susceptibility to decay and the cellulose content of different species. With these two seemingly possible conditions in mind, woods with extremely high densities, such as hickory, others with extremely low densities, as balsa, and some with intermediate specific gravity were selected. These woods are as follows:

Species	Where Obtained
Western yellow pine (*Pinus ponderosa*)	Coconino Co., Arizona
Yellow cedar (*Chamaecyparis nootkatensis*)	Snohomish Co., Washington
Incense cedar (*Libocedrus decurrens*)	Fresno Co., California
Tanbark oak (*Quercus densiflora*)	Trinity Co., California
Redwood (heartwood) (*Sequoia sempervirens*)	Shipment from Pacific Lumber Co., California
Mesquite (*Prosopis juliflora*)	Shipment from Board of Commissioners of Agriculture and Forestry, Division of Forestry, Honolulu, Hawaii
Balsa (*Ochroma lagopus*)	Shipment from American Balsa Co., New York
Shellbark hickory (*Hicoria ovata*)	Harrisonburg Co., Virginia

The results obtained from the analysis of the eight woods are given in Table I. In the analytical work, which followed the methods described by the former investigators, all samples except incense cedar and mesquite were run in duplicate. The results tabulated are the average of the two determinations. The data relative to redwood are not exactly comparable with the results obtained on the other species shown in Table I, as the sapwood showed decay, and the heartwood only could be analyzed.

Discussion of Results

Ash Content—The ash in the hardwoods runs considerably higher than in the conifers. Balsa, which weighs about 7 lbs. per cu. ft., has an unusually high ash content as compared with the other species listed in the table. Estimated on a ton basis, balsa would be a good source of potash, provided its ash is high in potassium. Measured on a cord basis, however, the yield of potash is lower than in other hardwoods.

Cold Water Soluble Content—The outstanding features of the cold water solubility determinations are shown in connection with mesquite and balsa. The former has an exceptionally high cold water-soluble content, owing to the mesquite gum. The latter has a low cold water-soluble content because it contains very little tannin or gum. The redwood runs fairly high in water-soluble material, undoubtedly because of the large amount of tannin.

Hot Water-Soluble Content—The hot water-soluble content is from 1 to 2.5 per cent higher than the cold water-soluble content. The hot water-soluble material of redwood is 9.86 per cent. This is considerably less than the tannin content of the same wood reported by Scalione.[7]

Ether-Soluble Content—The general idea prevails that the ether-soluble content is higher in conifers than in the hardwoods. Exceptions, however, are redwood among the conifers, and mesquite and balsa among the hardwoods. As would be expected, western yellow pine has the highest ether extract in this series of woods.

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[1] [illegible] Chemistry at the 63rd Meeting of the American Chemical Society, Birmingham, Ala., April 3 to 7, 1922.

[2] Published by permission of the Department of Agriculture.

[3] Chemist in Forest Products Laboratory, Madison, Wis.

[4] Assistant Chemist in Forest Products Laboratory, Madison, Wis.

[5] This Journal, 9 (1917), [illegible].

[6] Ibid., 12 (1920), [illegible]; 14 (1922), [illegible].

[7] This Journal, 11 (1919), 643.

TABLE I—ANALYSES OF WOODS

(Results in percentage of oven-dry (105° C.) samples)

				Solubility in											In Cellulose				
Species	Sample	Moisture	Ash	Cold Water	Hot Water	Ether	1 Per cent NaOH	Acetic Acid	Methoxy	Pentosan	Methyl Pentosan	Cellulose	Lignin	Pentosan	Methyl Pentosan	α-Cellulose	β-Cellulose	γ-Cellulose
Western yellow pine	141	5.32	0.43	5.58	5.67	9.63	22.08	0.92	4.55	8.06	1.68	56.22	26.75	[illegible]	2.13	69.18		30.82
(*Pinus ponderosa*)	142	8.28	0.42	2.97	3.40	6.52	16.58	1.24	4.02	9.96	[illegible]	57.72	25.85	8.97	1.97	66.17	5.52	28.31
	143	6.89	0.55	4.62	6.33	9.45	23.16	1.03	4.51	5.88	1.81	58.88	26.29	4.20	1.90	57.65	[illegible]	35.80
	144	5.19	0.44	3.17	4.89	6.48	19.37	1.18	4.87	5.52	1.77	56.82	27.72	4.63	1.90	55.40	19.02	25.58
	MEAN	6.42	0.46	4.09	5.05	8.52	20.30	1.09	4.49	7.35	1.62	57.41	26.65	6.82	1.98	62.10	10.56	30.13
Yellow cedar	161	3.54	0.33	1.66	2.89	2.67	13.80	1.66	5.42	8.86	3.97	51.45	33.21	8.60	2.03	62.88	11.10	26.02
(*Chamaecyparis*	162	5.19	0.35	3.03	3.46	3.34	14.49	1.62	5.60	8.52	3.57	54.04	31.27	8.09	1.91	62.96	10.99	26.05
nootkatensis)	163	4.87	0.62	2.47	2.86	2.08	12.69	1.55	5.05	6.72	2.97	54.78	30.43	6.65	1.65	59.37	11.64	28.97
	164	5.91	...	2.74	3.23	2.11	12.67	1.54	4.92	7.37	3.17	55.17	30.27	6.86	1.54	65.52	10.51	23.97
	MEAN	4.89	0.43	2.47	3.11	2.55	13.41	1.59	5.25	7.87	3.42	53.86	31.32	7.30	1.78	62.68	11.06	26.25
Incense cedar	165	5.32	0.38	3.09	4.87	3.33	17.37	0.96	6.34	11.07	1.20	39.94	38.14	9.53	2.13	48.47	15.42	36.11
(*Libocedrus*	166	4.63	0.27	2.53	3.62	4.69	13.81	1.04	6.29	9.99	1.60	44.10	37.73	7.90	1.71	41.42	12.77	45.81
decurrens)	167	5.42	0.38	5.31	7.64	4.90	21.89	0.73	6.09	10.70	1.26	40.76	37.17	9.83	2.13	50.90	6.82	42.28
	MEAN	5.12	0.34	3.64	5.38	4.31	17.69	0.91	6.24	10.65	1.35	41.60	37.68	9.08	1.99	46.92	11.67	41.06
Redwood (heartwood)	168	9.64	0.22	7.31	9.77	1.00	20.06	1.03	5.27	7.93	2.77	48.67	34.18	7.40	2.09	78.81	2.95	18.24
(*Sequoia sempervirens*)	168	9.71	0.20	7.40	9.94	1.14	19.94	1.13	5.16	7.67	2.74	48.23	34.25					
	MEAN	9.68	0.21	7.36	9.86	1.07	20.00	1.08	5.21	7.80	2.75	48.45	34.21	7.40	2.09	78.81	2.95	18.24
Tanbark oak	151	4.10	0.78	4.14	5.25	0.74	22.59	5.70	5.34	20.02	None	59.40	23.29	23.22	None	55.50	18.81[1]	25.64
(*Quercus densiflora*)	152	3.95	0.81	4.32	6.15	0.73	25.33	5.70	6.19	20.00	None	56.50	26.07	25.46	None	55.91	2.95	41.14
	153	3.26	0.82	4.22	5.92	0.80	23.91	4.40	5.35	19.13	None	57.27	25.20	20.30	None	58.15	22.62[1]	19.23
	154	3.36	0.91	3.72	5.08	0.98	22.93	5.13	6.09	19.22	None	58.95	24.86	22.32	None	57.82	18.27[1]	24.21
	MEAN	3.66	0.83	4.10	5.60	0.80	23.96	5.23	5.74	19.59	None	58.03	24.85	22.82	None	56.77	19.92	23.03
Mesquite	171	4.53	0.57	12.55	15.27	2.20	28.72	1.53	5.68	14.04	0.59	44.79	30.27	17.99	1.07	76.00	1.73	22.27
(*Prosopis juliflora*)	172	6.10	0.58	13.50	15.77		30.08	1.70	5.69	13.99	0.69	45.28	30.13	17.99	1.21	76.71	2.56	20.73
	173	6.15	0.49	12.68	15.56	2.33	29.60	2.53	5.29	13.85	1.18	45.87	31.28	17.57		76.40	2.06	21.54
	174	5.20	0.50	11.74	13.77	2.37	25.69	2.37	5.66	13.95	0.34	45.97	30.22	17.44	0.96	76.83	3.04	20.13
	MEAN	5.49	0.54	12.62	15.09	2.30	28.52	2.03	5.55	13.96	0.70	45.48	30.47	17.75	0.81	76.48	2.35	21.27
Balsa	175	6.50	2.15	1.85	2.84	1.27	20.37	5.75	5.71	17.51	0.88	54.04	26.52	19.99	1.35	75.64	0.27	24.08
(*Ochroma lagopus*)	175	6.44	2.09	1.68	2.74	1.19	20.36	5.85	5.65	17.79	0.83	54.24	26.47	...	...	...	...	...
	MEAN	6.47	2.12	1.77	2.79	1.23	20.37	5.80	5.68	17.65	0.86	54.15	26.50	19.99	1.35	75.64	0.27	24.08
Hickory (shellbark)	177	9.60	0.65	4.71	5.41	0.65	18.65	2.60	5.61	18.58	0.92	55.60	23.83	21.33	1.64	75.27	2.64	22.09
(*Hicoria ovata*)	178	7.39	0.74	4.86	5.73	0.62	19.44	2.42	5.65	19.06	0.67	56.85	23.04	22.45	1.19	77.38	3.01	18.61
	MEAN	8.49	0.69	4.78	5.57	0.63	19.04	2.51	5.63	18.82	0.80	56.22	23.44	21.89	1.41	76.32	2.82	20.35

[1] Trouble filtering.

ONE PER CENT NaOH-SOLUBLE CONTENT—The alkali-soluble extract consists primarily of tannins, resin acids, and carbohydrates, with slight traces of cellulose and lignin. The alkali-soluble material in western yellow pine and redwood averages above that of the other conifers. This is due to the high resin content of the former and the large percentage of tannin of the latter. Tanbark oak and mesquite among the hardwoods show a high percentage of alkali-soluble material.

METHOXY CONTENT—It will be noted that on the average the softwoods run slightly lower in methoxy content than the hardwoods. The one exception is incense cedar, which, on account of its exceedingly high methoxy content, might be expected to compare favorably with hardwoods for the production of methanol by destructive distillation. It has been found, however, that the conifers as a rule produce scarcely 30 per cent as much methanol as the hardwoods, even though their methoxy content is about 85 per cent of that in the broad-leaved species. Consequently, a very poor yield of methanol from incense cedar is not surprising. The above chemical constants are discussed more fully in connection with acetic acid content, as shown in Table II.

TABLE II—PERCENTAGES OF ACETIC ACID, METHOXY, AND METHANOL IN VARIOUS WOODS

	Acetic Acid		Methoxy and Methanol	
Species	Acid Hydrolysis	Destructive Distillation	Zeisel Method for Methoxy	Destructive Distillation for Methanol
Birch	4.30	6.80[1]	6.07	1.54[1]
Maple	4.46	5.26[1]	7.25	1.76[1]
Tanbark oak	5.23	6.89[1]	5.74	1.72[1]
Hickory	2.51	5.05[2]	5.63	2.08[2]
Redwood	1.08	...	5.21	...
Incense cedar	0.91	..	6.24	..

[1] U. S. Dept. Agr., Bull. 508.
[2] *Ibid.*, 129.

A higher yield of acetic acid is obtained in all cases by destructive distillation than by acid hydrolysis. The reverse is true in regard to methoxy and methanol.

PENTOSAN CONTENT—As in acetic acid content there is also a marked difference in the percentage of pentosans, presumably xylan and araban, in the softwoods and hardwoods. The analyses of the eight species examined show that the pentosan content of coniferous woods is about 50 per cent of that found in broad-leaved species. The average for the former is 8.4 per cent, for the latter 17.5 per cent.

METHYL PENTOSAN CONTENT—The percentage of methyl pentosans is considerably higher in softwoods than in hardwoods. Tanbark oak is the only one of all the species which contains no methyl pentosans. The quantity of pentosans and methyl pentosans obtained confirms the conclusions of Schorger[8] and of Mahood and Cable.[9]

CELLULOSE CONTENT—No marked difference in the cellulose content of hardwoods and softwoods appears to exist in the eight species analyzed. Of the hardwoods mesquite is low in cellulose, and of the softwoods, incense cedar and redwood have a low percentage of cellulose when compared with western yellow pine and yellow cedar. Cellulose was prepared according to the directions outlined by Schorger,[5] and is the residue left after the alternate chlorination and sodium sulfite extraction had been carried out until the sodium sulfite filtrate remained colorless.

That the cellulose thus obtained differs in individual species is apparent from the pentosan content of the cellulose from the various woods.

Calculated on the oven-dry weight of the wood, the cellulose isolated from the softwoods is from 4.5 to 5.0 per cent higher than the pentosan-free cellulose; in the hardwoods it is from 8.5 to 13.3 per cent higher. This is considering the pentosans and methyl pentosans collectively. If it were possible to extract the pentosans and nothing more from cellulose of various woods obtained by the Cross and Bevan method, one might argue that the residual material should

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[8] THIS JOURNAL, 9 (1917), 563.
[9] *Ibid.*, 14 (1922), 933.

TABLE III—DISTRIBUTION OF PENTOSANS
(Results in percentages of oven-dry weight of wood)

SPECIES	Cellulose in Wood (1)	Cellulose Pentosans in Wood (2)	Pentosan Free Cellulose in Wood (3)	α Cellulose in Wood (4)	β- + γ-Cellulose in Wood (5)	Hexosans in β- + γ-Cellulose (6)	Pentosans in α-Cellulose (7)	α-Cellulose Pentosans in Wood (8)	Per cent Cellulose Pentosans Retained in α-Cellulose (9)
W. y. pine	57.41	5.06	52.35	35.65	21.76	16.70	1.82	0.65	12.8
W. w. pine	59.71	4.34	55.37	38.57	21.14	16.80	2.05	0.79	18.2
Yellow cedar	53.86	4.89	48.97	33.76	20.10	15.21	..	..	..
Incense cedar	41.60	4.60	37.00	19.52	22.08	17.48	..	..	..
Redwood	48.45	4.60	43.85	38.10	10.35	5.75	..	..	..
Tanbark oak	58.03	13.24	44.79	32.94	25.09	11.85	9.51	3.13	23.6
Eucalyptus	57.62	13.49	44.13	39.66	17.96	4.47	..	..	..
Mesquite	45.48	8.48	37.00	35.61	9.87	1.39	3.48	1.24	14.6
Balsa	54.15	11.56	42.59	40.96	13.19	1.63	2.63	1.07	9.2
Hickory	56.22	13.10	43.12	42.92	13.30	0.20	..	..	..

Cotton (purified cellulose), 1.03 per cent pentosan

be the same. How such a separation can be accomplished cannot be answered by consulting our present methods of analysis. Even if a clean-cut separation of the pentosans from the rest of the cellulose were made, the remaining residues from the various woods seem to differ in some respects. This can be illustrated by using some of the data in Table I to obtain a different relationship, as shown in Table III. Column 2 shows the per cents of pentosans which resist the treatment for determining cellulose. The hardwood cellulose contains a much higher per cent of pentosans than the softwood cellulose. It was thought that a complete extraction of these bodies from the cellulose could be accomplished by using 17.5 per cent sodium hydroxide, as is done in separating alpha- from beta- and gamma-cellulose. If the figures in Column 4 are subtracted from the corresponding numbers in Column 1, the values of the beta- and gamma-cellulose in the various woods are obtained. In other words, the results in Column 5 represent the per cents of material extracted from cellulose with 17.5 per cent NaOH. Now, if the pentosans exist as such in the cellulose, one would expect a complete extraction of such bodies with 17.5 per cent NaOH, especially when it is noted that a large amount of hexosans is also dissolved with the treatment. In Column 6 is found the per cent of hexosans extracted over and above the per cent of pentosans present. On this basis, the per cents of hexosans dissolved in the first four woods agree favorably. In the tanbark oak also the amount of hexosans extracted is high. In the remaining five species the per cent of extract in excess of the pentosans present is low compared with the species mentioned above.

To determine whether all the pentosans are removed from the remaining cellulose by a 17.5 per cent NaOH treatment, samples of alpha-cellulose of western yellow pine, western white pine, tanbark oak, mesquite, balsa, and some purified cotton cellulose were subjected to the regular pentosan determination. The results given in Column 7 were obtained. Calculating these results on the oven-dry basis of the original wood as indicated in Column 8, and comparing those figures with the corresponding ones in Column 2, one may see that a considerable part of the pentosans found in the original wood is still retained in the alpha-cellulose. This is shown on a percentage basis in Column 9 of Table III. From these figures it is apparent that the alpha-cellulose isolated from the various sources is not the same chemically as is claimed by some investigators who have worked with too limited a number of samples.

It is realized that some will argue that the furfural found by distilling the alpha-cellulose with 12 per cent HCl might have been due to a breaking down of some hexoses formed by hydrolysis. It is claimed[10] that such sugars produce small amounts of furfural under the above conditions. According to the above reference, the per cent of furfural available from such a source is considerably lower than the figures of this table show.

Another source of furfural may be oxycellulose.[11] It is possible that some of this form of cellulose may be present when preparing the material according to the Cross and Bevan method. If the furfural found when working with alpha-cellulose in this research came from oxycellulose, then it should be possible to hydrolyze the alpha-cellulose to a hexose quantitatively. If, however, the furfural came from pentosans present in the alpha-cellulose, then it should be possible to identify some pentose derivatives after hydrolyzing the alpha-cellulose with acid. This work will be done later.

From the data presented in this paper it appears as though the celluloses prepared from the different sources are not identical. It is, perhaps, possible to reduce two or more of them to the same stable nucleus by alternate alkali and acid treatments. Whether this should be done or not depends upon just how cellulose should be defined. To the writer it seems that such a reduction is carrying the treatment to an extreme. By such a process it is possible to reduce two or more definite individual compounds to the same nucleus. For instance, benzoic acid and phthalic acid on treatment with lime produce benzene. Methyl benzene and ethyl benzene on oxidation give benzoic acid. In like manner it might be possible to change two or more definite kinds of cellulose to the same stable complex. The pentosans which withstand the vigorous treatment to which they are subjected in the Cross and Bevan process must without a doubt be closely bound with the cellulose molecule, if not really incorporated in it. If one refers to the work of Johnsen and Hovey,[12] in which they discuss the relative merits of the original and modified methods of Cross and Bevan for preparing cellulose, he will see that their work confirms what has been found by the writer. On page 44 of their report is found the following data:

TABLE IV—COMPARISON OF CELLULOSE OBTAINED IN CROSS AND BEVAN'S ORIGINAL AND MODIFIED METHODS

SPECIES	Cellulose, Per cent Original Method	Cellulose, Per cent Modified Method	Furfural in Cellulose Per cent Original Method	Furfural in Cellulose Per cent Modified Method
Balsam fir	54.45	51.50	5.43	4.39
Aspen	60.95	57.25	11.88	10.16

By recalculation and rearrangement of these data, the following results are obtained:

TABLE V—FURFURAL AND PENTOSANS OF ORIGINAL WOOD IN THE CELLULOSE
(Percentages are based on weight of the original wood)

SPECIES	Original Method	Modified Method	Loss in Cellulose	Loss in Furfural	Loss in Pentosans	Loss in Hexosans
Balsam fir	54.45	51.50	2.95	0.63	0.98	1.97
Aspen	60.95	57.25	3.70	1.43	2.23	1.47

If the furfural in Column 4 comes from pentosans, then the figures in Column 5 indicate the amount of pentosans extracted. By subtracting the data in Column 5 from the

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[10] Browne, "Handbook of Sugar Analysis," p. 453.

[11] Browne, "Handbook of Sugar Analysis," p. 376.

[12] *Paper*, **21** (1917–18), 36.

TABLE VI.—ANALYSES OF WOODS

(Results in percentage of oven-dry (105° C.) samples)

				Solubility in										In Cellulose				
Species	Sample	Moisture	Ash	Cold Water	Hot Water	Ether	1 Per cent NaOH	Acetic Acid	Methoxy	Pentosan	Methyl Pentosan	Cellulose	Lignin	Pentosan	Methyl Pentosan	α Cellulose	β Cellulose	γ Cellulose
Western yellow pine (*Pinus ponderosa*)	141	5.32	0.43	5.58	5.67	9.63	22.08	0.92	4.55	8.06	1.68	56.22	26.75	[illegible]	2.13	69.18	...	30.82
	142	8.28	0.42	2.97	3.40	6.52	16.58	1.24	4.02	9.96	1.24	57.72	25.85	8.97	1.97	66.17	5.52	28.31
	143	6.89	0.55	4.62	6.33	9.45	23.16	1.03	4.51	5.88	1.81	58.88	26.29	4.20	1.90	57.65	6.54	35.80
	144	5.19	0.44	3.17	4.89	6.48	19.37	1.18	4.87	5.52	1.77	56.82	27.72	4.63	1.90	55.40	19.62	[illegible]
	Mean	6.42	0.46	4.09	5.05	8.52	20.30	1.09	4.49	7.35	1.62	57.41	26.65	6.82	1.98	62.10	10.56	30.13
Yellow cedar (*Chamaecyparis nootkatensis*)	161	3.54	0.33	1.66	2.89	2.67	13.80	1.66	5.42	8.86	3.97	51.45	33.21	8.60	2.03	62.88	11.10	26.02
	162	5.19	0.35	3.03	3.46	3.34	14.49	1.62	5.60	8.52	3.57	54.04	31.27	8.09	1.90	62.96	10.99	26.05
	163	4.87	0.62	2.47	2.86	2.08	12.69	1.55	5.05	6.72	2.97	54.78	30.43	6.65	1.65	59.37	11.64	28.97
	164	5.91	...	2.74	3.23	2.11	12.67	1.54	4.92	7.37	3.17	55.17	30.27	5.86	1.54	65.52	10.51	23.97
	Mean	4.89	0.43	2.47	3.11	2.55	13.41	1.59	5.25	7.87	3.42	53.86	31.32	7.30	1.78	62.68	11.06	26.25
Incense cedar (*Libocedrus decurrens*)	165	5.32	0.38	3.09	4.87	3.33	17.37	0.96	6.34	11.07	1.20	39.94	38.14	9.53	2.13	48.47	15.42	36.11
	166	4.63	0.27	2.53	3.62	4.69	13.81	1.04	6.29	9.99	1.60	44.10	37.73	7.90	1.71	41.42	12.77	45.81
	167	5.42	0.38	5.31	7.64	4.90	21.89	0.73	6.09	10.70	1.26	40.76	37.17	9.83	2.13	50.90	6.82	42.28
	Mean	5.12	0.34	3.64	5.38	4.31	17.69	0.91	6.24	10.65	1.35	41.60	37.68	9.08	1.99	46.92	11.67	41.06
Redwood (heartwood) (*Sequoia sempervirens*)	168	9.64	0.22	7.31	9.77	1.00	20.06	1.03	5.27	7.93	2.77	48.67	34.18	7.40	2.09	78.81	2.95	18.24
	168	9.71	0.20	7.40	9.94	1.14	19.94	1.13	5.16	7.67	2.74	48.23	34.25	...	...	...	...	...
	Mean	9.68	0.21	7.36	9.86	1.07	20.00	1.08	5.21	7.80	2.75	48.45	34.21	7.40	2.09	78.81	2.95	18.24
Western white pine[1] (*Pinus monticola*)	1	6.18	0.21	2.60	3.35	4.00	13.97	1.21	4.38	6.75	3.41	58.53	27.22	4.47	1.59	70.58	18.16	11.26
	2	7.68	0.20	1.73	2.57	4.42	12.70	0.94	4.59	7.19	3.25	62.29	24.15	5.68	2.97	64.31	10.69	24.97
	3	7.00	0.18	3.92	7.25	3.98	15.92	1.37	4.86	6.48	3.33	59.40	27.55	5.19	1.68	74.29	9.17	16.54
	4	7.15	0.19	4.40	4.78	4.63	16.51	1.09	4.41	7.46	2.90	58.61	26.82	5.96	1.56	49.27	27.27	23.46
	Mean	7.00	0.20	3.16	4.49	4.26	14.78	1.03	4.56	6.97	3.22	59.71	26.44	5.33	1.95	64.61	16.32	19.06
Longleaf pine[2] (*Pinus palustris*)	11	..	0.40	7.75	8.20	6.70	24.62	0.70	5.00	7.33	3.48	55.33	...	8.38	1.26			...
	12	..	0.34	5.60	6.03	6.70	21.07	0.93	4.90	7.52	3.29	57.53	...	7.19	1.39			
	13	..	0.35	5.40	6.78	2.65	18.89	0.62	5.26	7.57	3.87	61.41		7.39	1.03	...		
	20	..	0.38	6.05	7.57	9.23	24.87	0.79	5.03	7.43	3.67	59.67	...	7.90	0.96	...		
	Mean	..	0.37	6.20	7.15	6.32	22.36	0.76	5.05	7.46	3.60	58.48		7.71	1.16	...		
Douglas fir[2] (*Pseudotsuga taxifolia*)	1	..	0.40	3.79	6.62	0.94	15.82	0.93	4.81	6.03	4.24	61.97		5.56	1.26	...	...	...
	2	..	0.37	3.16	6.07	1.00	16.76	1.01	5.17	6.30	4.64	57.00		...	...	...	...	...
	3	..	0.35	2.94	6.36	1.11	15.12	1.13	4.88	6.00	4.38	63.08	...	...		...	...	...
	5	..	0.38	4.25	6.96	1.02	16.72	1.07	4.92	5.73	4.38	63.82		5.12	1.15	...	...	...
	Mean	..	0.38	3.54	6.50	1.02	16.11	1.04	4.95	6.02	4.41	61.47	...	5.34	1.20	...	...	...
Western larch[2] (*Larix occidentalis*)	1	..	0.21	10.45	12.57	0.72	22.07	0.61	5.08	11.15	2.47	58.25	...	9.12	1.40	...	...	...
	2	..	0.32	11.00	12.40	0.74	21.93	0.91	4.91	11.04	2.83	58.71	...	8.41	1.22	...		...
	3	..	0.22	8.16	10.08	0.93	19.44	0.76	5.08	10.22	3.14	60.91	...	8.67	1.24	...	...	
	4	..	0.16	12.83	15.30	0.83	25.11	0.55	5.05	10.78	2.80	53.31	...	9.55	0.90	...	...	
	Mean	..	0.23	10.61	12.59	0.81	22.14	0.71	5.03	10.80	2.81	57.80	...	8.94	1.19	...	...	...
White spruce[2] (*Picea canadensis*)	1	..	0.33	1.28	1.88	1.95	11.33	1.58	5.31	10.78	3.08	62.61		10.26	0.83	...		...
	2	..	0.29	0.92	2.28	0.90	11.58	1.57	5.26	10.31	3.52	63.29	...	9.29	0.68	...	...	...
	3	..	0.30	1.45	2.52	0.97	12.75	1.49	5.29	10.04	3.95	60.43	...	...	...	...		...
	4	..	0.32	0.82	1.88	1.63	10.63	1.73	5.32	10.42	3.64	61.09	...	9.33	0.66	...		
	Mean	..	0.31	1.12	2.14	1.36	11.57	1.59	5.30	10.39	3.55	61.85	...	9.63	0.72	...	...	...
Tanbark oak (*Quercus densiflora*)	151	4.10	0.78	4.14	5.25	0.74	22.59	5.70	5.34	20.02	...	59.40	23.29	23.22	...	55.50	18.81[1]	25.64
	152	3.95	0.81	4.32	6.15	0.73	25.33	5.70	6.19	20.00	...	56.50	26.07	25.46	...	55.91	2.95	41.14
	153	3.26	0.82	4.22	5.92	0.80	23.91	4.40	5.35	19.13	...	57.27	25.20	20.30	...	58.15	22.62[3]	19.23
	154	3.36	0.91	3.72	5.08	0.98	22.93	5.13	6.09	19.22	...	58.95	24.86	22.32	...	57.82	18.27[3]	24.21
	Mean	3.66	0.83	4.10	5.60	0.80	23.96	5.23	5.74	19.59	...	58.03	24.85	22.82	...	56.77	19.92	23.03
Mesquite (*Prosopis juliflora*)	171	4.53	0.57	12.55	15.27	2.20	28.72	1.53	5.68	14.04	0.59	44.79	30.27	17.99	1.07	76.00	1.73	22.27
	172	6.10	0.58	13.50	15.77	...	30.08	1.70	5.69	13.99	0.69	45.28	30.13	17.99	1.21	76.71	2.56	20.73
	173	6.15	0.49	12.68	15.56	2.33	29.60	2.53	5.29	13.85	1.18	45.87	31.28	17.57	...	76.40	2.06	21.54
	174	5.20	0.50	11.74	13.77	2.37	25.69	2.37	5.66	13.95	0.34	45.97	30.22	17.44	0.96	76.83	3.04	20.13
	Mean	5.49	0.54	12.62	15.09	2.30	28.52	2.03	5.55	13.96	0.70	45.48	30.47	17.75	0.81	76.48	2.35	21.17
Balsa (*Ochroma lagopus*)	175	5.50	2.15	1.85	2.84	1.27	20.37	5.75	5.71	17.51	0.88	54.04	26.52	19.99	1.35	75.64	0.27	24.08
	175	6.44	2.09	1.68	2.74	1.19	20.36	5.85	5.65	17.79	0.83	54.24	26.47	...	...	...	...	...
	Mean	6.47	2.12	1.77	2.79	1.23	20.37	5.80	5.68	17.65	0.86	54.15	26.50	19.99	1.35	75.64	0.27	24.08
Hickory (shellbark) (*Hicoria ovata*)	177	9.60	0.65	4.71	5.41	0.65	18.65	2.60	5.61	18.58	0.92	55.60	23.83	21.33	1.64	75.27	2.64	22.09
	178	7.39	0.74	4.86	5.73	0.62	19.44	2.42	5.65	19.06	0.67	56.85	23.04	22.45	1.19	77.38	3.01	18.61
	Mean	8.49	0.69	4.78	5.57	0.63	19.04	2.51	5.63	18.82	0.80	56.22	23.44	21.89	1.41	76.32	2.82	20.35
Eucalyptus[1] (*Eucalyptus globulus*)	1	6.99	0.23	2.65	4.41	0.54	16.57	2.31	7.11	21.41	1.97	59.67	24.04	20.35	3.92	67.85	2.11	31.04
	2	6.55	0.20	4.93	6.96	0.52	18.42	1.97	6.37	20.66	2.14	58.53	25.24	21.62	2.44	69.75	0.00	31.25
	3	6.87	0.27	5.31	8.26	0.60	17.90	1.51	6.87	17.90	2.74	56.45	25.07	20.10	2.24	68.99	0.00	31.01
	4	5.90	0.24	5.79	8.27	0.59	21.40	1.62	6.56	20.39	2.48	55.83	26.74	21.76	1.26	...	...	...
	Mean	6.58	0.24	4.67	6.98	0.56	18.57	1.85	6.73	20.09	2.33	57.62	25.07	20.96	2.46	68.86	0.70	31.10
Basswood[2] (*Tilia americana*)	1	..	0.80	2.04	3.84	1.50	23.43	5.78	6.23	19.82	3.72	62.92	...	24.48	1.19	...	...	...
	2	..	0.74	1.63	2.94	1.14	21.61	6.14	6.05	19.54	3.85	62.41	...	23.54	1.46	...		...
	3	..	0.96	3.14	5.66	3.59	26.93	5.46	6.11	20.37	3.68	54.66	...	26.61	1.62	...	...	...
	4	..	0.94	1.23	3.22	0.89	21.46	5.41	5.91	19.14	4.16	63.13	...	21.89	1.45	...		...
	5	..	0.85	2.55	4.67	2.68	25.38	6.18	5.72	20.79	3.23	63.08	...	24.86	2.00		...	...
	Mean	..	0.86	2.12	4.07	1.96	23.76	5.79	6.00	19.93	3.73	61.24	...	24.28	1.54	...	...	...
Yellow birch[2] (*Betula lutea*)	1	..	0.58	2.88	4.21	0.55	20.02	3.99	6.12	24.26	3.18	60.49	...	28.40	1.11	...	...	...
	2	..	0.57	2.58	3.87	0.67	20.20	4.39	6.03	25.40	3.12	61.08	...	29.96	1.32	...	...	...
	3	..	0.54	3.15	4.66	0.54	19.51	3.81	6.19	23.00	2.25	61.82		26.55	1.04			...
	4	..	0.37	2.06	3.15	0.63	19.65	5.02	5.92	25.86	2.21	61.85	...	...	...			
	Mean	..	0.52	2.67	3.97	0.60	19.85	4.30	6.07	24.63	2.69	61.31	...	28.30	1.16			...
Sugar maple[2] (*Acer saccharum*)	1	..	0.46	2.60	4.27	0.29	16.98	4.26	7.22	21.10	2.50	60.78	...	21.08	1.04		...	...
	2	..	0.51	2.73	4.22	0.22	17.20	4.25	7.23	21.90	2.14	61.67	...	25.82	1.05		...	...
	3	..	0.40	2.94	4.78	0.30	18.04	4.60	7.25	22.21	2.05	60.20	...	25.83	1.00			
	4	..	0.38	2.33	4.15	0.20	18.35	4.74	7.28	21.62	2.85	60.48		25.20	0.77			
	Mean	..	0.44	2.65	4.36	0.25	17.64	4.46	7.25	21.71	2.39	60.78	...	24.48	0.96	...	...	...

[1] THIS JOURNAL, 14 (1922), 933.

[2] *Ibid.*, 9 (1917), 556

[3] Trouble Filtering.

corresponding items in Column 3, the substances other than pentosans (hexosans) are indicated. In each case there is a considerable amount of such substances removed from the cellulose. Until a uniform method of isolating cellulose is decided upon, the material which different investigators prepare from the same source will undoubtedly have varying characteristics when subjected to chemical tests. If such a complex substance as cellulose prepared by a uniform method from different sources is not identical, there ought not be any cause for concern, for it might be possible that more than one kind of the substance does exist.

LIGNIN CONTENT—There is no marked distinction in the lignin content of hardwoods and softwoods. If western yellow pine and mesquite are eliminated from the eight species analyzed, it then appears as though, on the average, the softwoods have a higher lignin content than the hardwoods. A larger number of species must be analyzed, however, before a definite conclusion can be drawn.

Contrary to some experimental data, it is generally accepted that the methoxy group is entirely associated with the lignin. If this were the case, either of the following conditions should obtain: (1) The lignin content should be proportional to the methoxy content in the various species; or (2) the composition of the lignin in different species must vary.

A case in which the total methoxy content of the wood is recovered from the isolated lignin is found in a paper by Dore[13] on "The Distribution of Certain Chemical Constants of Wood over Its Proximate Constituents." In this paper it was found that the methoxy content of redwood is 5.60 per cent. By determining the methoxy content of the redwood lignin, Dore was able to recover the entire methoxy found in the original wood.

In another paper by the same author,[14] on "The Approximate Analysis of Hardwoods," is found some data showing that in live oak the methoxy is only partially associated with the lignin. The methoxy content of the original oven-dry live oak was found to be 5.80 per cent. Of this amount 3.72 per cent was associated with the live-oak lignin. The remaining 2.08 per cent methoxy was found to be otherwise associated or, at most, loosely associated with the lignin. This, then, is an example in which more than one-third of the total methoxy content of the original wood is not found in the isolated lignin. That the methoxy is not entirely associated with the lignin in hardwoods, and firmly bound to the lignin in softwoods, seems to be shown by the above example. Whether this condition is true of hardwoods and softwoods generally, is a study which will be taken up at the Forest Products Laboratory in the future. As is shown in Table I, the methoxy content is not proportional to lignin. The proportion between the two chemical constants does not even hold in a series of woods belonging to either the hardwood or softwood classes.

It is of interest to use the data on redwood and live oak and calculate the methoxy content of the redwood and live-oak lignins. Following are the results:

Species	CH$_3$O Content Oven-Dry Wood Per cent	CH$_3$O Content Oven Dry Wood in Lignin Per cent	Lignin Content of Oven Dry Wood Per cent	CH$_3$O Content of Lignin Per cent
Redwood	6.25	6.28	34.5	18.17
Live oak	5.80	3.72	21.14	17.59

From this table it appears that the composition of lignin in the two species is quite uniform from the standpoint of methoxy content. If this uniformity of the methoxy content of lignin holds in all woods, then the methoxy not associated with the lignin must vary. This is another project which will be investigated in connection with per cent of total methoxy associated with the lignin, to which reference was made above.

It is an experimental fact that softwoods do not react the same as hardwoods from the standpoint of methanol yield, when subjected to destructive distillation. If the softwoods have all the methoxy associated with the lignin, and the hardwoods only a part, as the very limited amount of data show, it may explain why the broad-leaved species give higher yields of methanol. It is possible that the methoxy not combined with lignin is more easily obtained as methanol than the methoxy associated with lignin. Under such conditions, the greater share of methanol in hardwoods would be derived from methoxy not associated with the lignin. In softwoods it would originate from the lignin methoxy entirely.

PENTOSANS AND METHYL PENTOSANS IN CELLULOSE—From 38 to 56 per cent of the pentosans and methyl pentosans of the original wood are retained in the softwood cellulose and from 57 to 66 per cent in the hardwood cellulose. The hardwood cellulose is higher in pentosans, and lower in methyl pentosans, than softwood cellulose. The relationship between these pentose-producing bodies in the hardwood and softwood celluloses is similar to that found in the original species.

ALPHA-, BETA-, AND GAMMA-CELLULOSE—This determination is of interest to the manufacturers of soda and sulfate pulps and cellulose derivatives, who wish a high yield of stable or alpha-cellulose.

The conifers have a higher gamma-cellulose content than the deciduous class.

DENSITY AND CHEMICAL COMPOSITION—By comparing the chemical composition of a dense wood, such as hickory, with a light wood, such as balsa, the only striking differences in chemical constants which might affect density are water-soluble content, cellulose, and lignin. The higher water extract in hickory should tend to increase its density. The slight differences in Table I in the cellulose and lignin content of the two woods should not affect the density. Therefore, specific gravity seems to depend upon structure—that is, compactness of the cells and the quantity of extractive material.

CELLULOSE CONTENT AND RESISTANCE TO DECAY—Balsa, on account of its extreme lightness, is used in the manufacture of life-saving apparatus and insulating material. The wood must be treated chemically to protect it against water-soaking and decay. Its extreme susceptibility to decay is claimed to be due to a very high cellulose content. The results found in its analysis show that the cellulose content of balsa is not above the average of other woods. Therefore, the ease with which balsa decays seems to be due to some other specific property.

ANALYSES OF WOODS—Table VI includes the data on the species referred to in this report, as well as that previously published by the Forest Products Laboratory on the comparative chemical composition of woods. The results are derived from the three sources indicated in the footnotes.

By consulting the directions of Schorger and Mahood for preparing the wood sample for determining cellulose, it will be noted that a change was made by the latter. The directions of Mahood were followed in the cellulose determinations given in this paper.

Abstracts of Pittsburgh Papers

The A. C. S. News Service has on hand a limited number of sets of such abstracts as were submitted prior to the Pittsburgh meeting. It has come to our notice that some of the members would like to have these abstracts prior to the publication of the papers, and they are therefore offered, while the supply lasts, at $1.00 per set. This sum is to cover postage and a part of the expense involved in their preparation.

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[13] This Journal, 12 [illegible]

[14] Ibid., 12 (1920), [illegible]

Distribution of Methoxyl in the Products of Wood Distillation[1,2,3]

By L. F. Hawley[4] and S. S. Aiyar

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Methoxyl groups in wood are the source of the methanol obtained by destructive distillation, but only 16 to 30 per cent of the methoxyl goes to form methanol. This paper describes the search for the other 84 to 70 per cent methoxyl in the crude products of distillation of maple, oak, and incense cedar. The changes in the distribution of the methoxyl when the wood is treated with sodium carbonate or phosphoric acid before distillation are also described.

IT HAS been shown that methoxyl groups occur in wood in greater amount than is equivalent to the methanol obtained by the destructive distillation of the same kind of wood.[5] It has also been shown that the methanol obtained by distillation can be increased by treating the wood with certain chemicals before distillation.[6] In order to find the location of the excess methoxyl not used in forming methanol and to determine the source of the increase in methanol when the wood is treated with chemicals before distillation, this work was undertaken.

The general plan was to determine methoxyl in a sample of wood and then distil the wood, either with or without previous chemical treatment, and determine methoxyl in the various crude products, settled tar, dissolved tar, tar-free pyroligneous acid, charcoal, and gas. It was assumed that the methane in the gas represented an equivalent amount of methoxyl in the original wood. This assumption seems to be safe in view of the rough relationship between the amount of methoxyl in a cellulosic material and the amount of methane in the gas obtained on distillation.

DETERMINATION OF METHANE

Several publications have given information on the amount of methane formed by the destructive distillation of wood and cellulose. Klason, von Heidenstam, and Norlin[7] showed that wood gave considerable amounts of methane, while cellulose from cotton, fir, and pine gave only about 0.27 per cent methane. Bantlin[8] distilled cellulose of unknown origin and obtained 0.68 per cent methane. Sarasin[9] reported only traces of methane from cotton cellulose. These agree fairly well, but Erdmann and Schaefer[10] reported 19 per cent methane in the gas from the distillation of cellulose. The percentage of gas on the cellulose distilled was not given, but even with a conservative estimate of 12 per cent gas the methane would be 2.3 per cent, which is very much higher than that found by others. In order to settle this point and to determine the amount of methane formed from celluloses of known methoxyl content, the distillations shown in Table I were made.

It is seen that the methane is slightly greater in amount than can be accounted for by the methoxyl in the original material, but the amounts are so small that no relationship can be established. The results agree with those of the previous authors, except Erdmann and Schaefer, who are apparently incorrect. There is, then, a rough relation between the amount of methoxyl in a cellulosic material and the amount of methane obtained by destructive distillation, so that at least a large part of the methane must come from methoxyl.

TABLE I—METHANE FORMED BY DISTILLATION OF CELLULOSES WITH KNOWN AMOUNTS OF METHOXYL

KIND OF CELLULOSE	Methoxyl Content	Methane Per cent on Original Cellulose	Equivalent of Methane in Terms of Methoxyl
Birch soda pulp............	0.225	0.20	0.40
Absorbent cotton...........	0.277	0.26	0.52
Spruce sulfite pulp (bleached)	0.342	0.17	0.34

The wood in the form of sawdust was distilled in a glass flask, and after condensation of the vapors the gases were passed through a wash bottle containing potassium hydroxide to remove most of the carbon dioxide, and then collected in a gasometer. Since only the methane and not the total gas was required, the removal of the carbon dioxide before measurement of the gas volume was permissible, and in this way the amount of gas to be collected and measured was considerably reduced.

METHOXYL DETERMINATIONS

The methoxyl determinations were made by the Zeisel method, which has been used for all the analyses of wood and wood products made at the Forest Products Laboratory. According to Klason[11] this method may give too high results when used with wood, on account of the formation of ethyl iodide from the —CH_2CH_2OH group in lignin, but this error amounts to very little and does not affect the conclusions to be drawn from this work. It is also possible that some methoxyl is formed from methyl groups like those in the methyl pentosans.

In the gas analysis care was taken to remove all carbon monoxide before determining the methane by the explosion method. Two cuprous chloride pipets were used, the second of which always contained a fresh solution, which had been used only for removing the last traces of carbon monoxide not absorbed by the first pipet.

Table II gives the results of such distillations and analyses on three different species, both without treatment and after treatment with different amounts of sodium carbonate or phosphoric acid. All the results are the averages of at least two distillations. The blank runs show the normal distribution of methoxyl groups in the products of distillation. In the case of maple the largest amount of methoxyl in any one product is found in the pyroligneous acid, and this represents very closely the methanol formed. The next

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[1] Presented before the Section of Cellulose Chemistry at the 63rd Meeting of the American Chemical Society, Birmingham, Ala., April 3 to 7, 1922.

[2] Published by permission of the Department of Agriculture.

[3] This communication is an abstract of a thesis submitted by the junior author in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the University of Wisconsin.

[4] In charge, Section of Derived Products, Forest Products Laboratory, Madison, Wisconsin.

[5] Schorger, THIS JOURNAL, **9** (1917), 556.

[6] Palmer, *Ibid.*, **10** (1918), 264; Hawley, *Ibid.*, **14** (1922), 43.

[7] *Arkiv Kemi. Mineral. Geol.*, **3** (1908), 1; *Z. angew. Chem.*, **22** (1909), 1205.

[8] *J. Gasbel.*, **57** (1914), 32, 55.

[9] *Arch. sci. phys. nat.*, [4] **46** (1921), 5.

[10] *Ber.*, **43** (1910), 2398.

[11] "Papperstidning," **1920**, p. 319.

TABLE II—DISTRIBUTION OF METHOXYL IN PRODUCTS OF WOOD DISTILLATION

(All figures in percentages of dry weight of wood distilled)

	Hard maple (6.09 per cent $-OCH_3$)				White oak (5.12 per cent $-OCH_3$)						Incense cedar (5.9 per cent $-OCH_3$)	
		Na_2CO_3				Na_2CO_3			H_3PO_4			Na_2CO_3
PRODUCTS	Blank	0.5%	1%	1.5%	Blank	0.5%	1%	1%	1.5%	3%	Blank	1%
Pyroligneous acid (tar free)	1.62	1.73	1.92	1.91	1.16	1.61	1.84	1.67	1.76	1.82	0.97	1.45
Dissolved tar	0.34	0.23	0.21	0.22	0.22	0.21	0.16	0.11	0.08	0.06	0.10	0.07
Settled tar	0.52	0.60	0.59	0.59	0.46	0.56	0.60	0.12	0.13	0.02	1.04	0.84
Charcoal	0.28	0.06	0.04	0.04	0.70	0.52	0.13	0.57	0.76	0.49	0.45	0.12
Gas (calc. from CH_4)	1.31	1.23	1.47	1.34	1.34	0.90	0.78	0.40	0.40	0.21	1.60	1.17
Total methoxyl recovered	4.07	3.85	4.23	4.10	3.88	3.80	3.51	2.87	3.13	2.60	4.16	3.70

largest amount of methoxyl is represented by the methane in the gas, and the other three products contain only small amounts of methoxyl. The total methoxyl found in the products is only about two-thirds that in the original wood and it seemed at first impossible to account for the other one-third. The slight error in the methoxyl determination in the original wood[11] might be the cause of an apparent loss of this kind, but such an error would amount to only a few tenths of a per cent. After the experimental work was all finished, a probable explanation of this apparent loss was discovered. In "Om Träkolning," by Bergstrom and Wesslén (Stockholm, 1918), is shown the composition of the gas given off when commercial charcoal is heated to temperatures above those at which it was originally produced from the wood. Large quantities of gas are given off from 450° to 900° C., and a large proportion of this gas is methane. Comparative figures are not available to show whether this methane is produced in just the right amount to account for the difference between the methoxyl in the original wood and in the distillation products as shown in Table I, but it is as near as could be expected with different species of wood and different methods of distillation, being about 2.1 per cent of the weight of the wood from which the charcoal was produced.

If this methane is formed from methoxyl groups in the charcoal, some explanation is required of the small amount of methoxyl found in the charcoal by analysis. It may be that the charcoal is so complex and most of the methoxyl so condensed that only a small part of the possible methyl iodide is formed by the action of hydriodic acid. This is the assumption made in the further discussions, and when "methoxyl in the charcoal" is mentioned only the methoxyl determined by the method of analysis is included.

MAPLE—When the maple sawdust was treated with sodium carbonate solution before distillation, the total methoxyl recovered was not greatly changed but the distribution was different. The pyroligneous acid contained more methoxyl (increase in methanol), and this increase is about equal to the decrease of methoxyl in the charcoal and the dissolved tar.

WHITE OAK—In the case of white oak, the methoxyl in the pyroligneous acid is low corresponding with the low yield of methanol from this species, and more methoxyl is accounted for in the gas than in the pyroligneous acid. When the white oak is treated with sodium carbonate solution before distillation, the methanol is increased, but this increase is not quite equaled by the decrease in the dissolved tar and charcoal. There is with this species, however, a marked decrease in the methane in the gas due to the addition of the sodium carbonate, and this decrease is sufficient to furnish the additional methoxyl required for the methanol increase.

A similar increase is found in the methanol when phosphoric acid is added to the wood before distillation. In this case, however, the decrease in the charcoal is not so great, but the decrease is much greater in all the other products, the total recovered methoxyl being only two-thirds as much with 3 per cent phosphoric acid as with the untreated wood. The decrease of methoxyl in the settled tar is due more to a decrease in the amount of the tar[12] than to a change in the composition of the tar.

INCENSE CEDAR—A softwood was included in this study, since softwoods give a lower proportion of their methoxyl in the form of methanol on distillation, and the distribution of methoxyl must, therefore, be different. Incense cedar was chosen as it contains an unusually large amount of methoxyl for a softwood. With this species not only the gas but also the tar contains more methoxyl than the pyroligneous acid, in contrast to the hard maple which gives more methoxyl in the pyroligneous acid than in any other product. When distilled after treatment with 1 per cent sodium carbonate, the effect is very much the same as in the case of oak—the methoxyl is increased in the pyroligneous acid, not much changed in the dissolved tar, and decreased in the charcoal and gas. The decrease in the charcoal and gas is more than enough to account for the increase in the pyroligneous acid.

TABLE III—TOTAL VOLATILE ACIDS

(All figures in per cent of dry weight of wood distilled)

		Sodium Carbonate			Phosphoric Acid		
SPECIES	Blank	0.5%	1%	1.5%	1%	1.5%	3%
Maple	4.94	4.32	4.04	4.10	..	..	..
White oak	3.88	3.93	3.81	..	3.24	3.15	2.87
Incense cedar	2.17	..	1.87	..	..	..	..

The yields of total acids obtained during these distillations are given in Table III. These acid yields, as well as the methoxyl yields in the pyroligneous acid, do not agree very well with the acid and alcohol yields, respectively, reported by Palmer and by Hawley,[6] but the conditions of distillation were different and there may have been differences in the samples of wood used even when the species were the same. It must also be remembered that the figures for methoxyl in the pyroligneous acid may not be the exact equivalent of the methanol as determined by specific gravity. The increase in alcohol yields due to phosphoric acid, as reported by Palmer, has been confirmed, although on another species of wood, but a decrease in acid was found contrary to Palmer's results. The increases in alcohol due to treatment with sodium carbonate are not so great as those reported previously,[6] but the acid yields for oak wood were not decreased by this treatment.

CONCLUSION

The methane in wood gas is formed largely from the methoxyl groups in the original wood.

Wood charcoal contains a small proportion of methoxy-groups which respond to the Zeisel method of analysis, and probably a much larger proportion which form methane when the charcoal is heated from 450° to 900° C.

Softwoods give more methoxyl in the settled tar and more methane in the gas than hardwoods, and these increases make up for the less methoxyl in the pyroligneous acid (small yield of methanol).

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[12] Palmer, THIS JOURNAL, **10** (1918), 264.

On distilling maple wood which has been treated with sodium carbonate, the increase in methanol is balanced by a decrease of methoxyl in the charcoal and dissolved tar.

On distilling white oak wood, which has been treated with sodium carbonate, the increase in methanol is balanced only by including some of the decrease of methane in the gas.

Phosphoric acid treatment of oak wood before distillation also increases the methanol but decreases the methoxyl in all the other crude products of distillation.

The effects of treatment with sodium carbonate are the same in the case of incense cedar as with oak, except that in the first case the methoxyl in the settled tar is decreased.

The Determination of Metallic Iron in Sponge Iron[1]

By Clyde E. Williams and Arvid E. Anderson[2]

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A method has been described by which the metallic iron in sponge iron can be determined accurately and rapidly.

The methods commonly employed for determining the copper-precipitating value are satisfactory for that purpose if they are performed under conditions that hold in plant operation, but, in most cases, they are not satisfactory for determining the metallic iron content.

When a copper sulfate solution is treated with metallic iron, more than an equivalent weight of copper is precipitated if the solution is either neutral or contains less than 0.075 sulfuric acid, whereas less than an equivalent weight of copper is precipitated if the solution contains more than 0.075 per cent sulfuric acid.

In the method described, precipitation of the copper from a neutral solution is preferred, but the acidity of the solution is not important unless it be sufficiently great to cause solution of any oxide of iron that might be present.

Sulfur, present as ferrous sulfide, causes high results in this and the other methods discussed.

The method here described for the determination of metallic iron in sponge iron was developed in connection with some experiments on the production of sponge iron that are being conducted at the Northwest Experiment Station of the U. S. Bureau of Mines, in coöperation with the College of Mines, University of Washington.

The production of sponge iron by the reduction of iron oxide at a low temperature is engaging the attention of many experimenters. Iron and steel metallurgists want sponge iron for subsequent conversion into foundry iron or steel, and copper metallurgists want it for precipitating copper from solutions resulting from leaching operations. Both are interested in the metallic iron content of the sponge iron, although the copper metallurgists have been satisfied with the "copper-precipitating value"—that is, the amount of copper that is precipitated by a unit quantity of the sponge iron. Methods for determining the metallic iron in *ferrum reductum* (a pharmaceutical and chemical reagent obtained by the reduction of pure iron oxide with hydrogen) have been used for years and should apply equally well for sponge iron.

Review of Methods Commonly Employed

Some of the important methods that have been used for determining metallic iron are the following:

(1) The Copper Sulfate Method—The copper sulfate method has been used for determining the copper-precipitating value of sponge iron, the metallic iron in sponge iron, and the metallic iron in *ferrum reductum*. In this method the sample is digested with copper sulfate solution and the amount of copper that has been precipitated is determined by analyzing either the precipitate or the filtrate for copper. The following equation represents the reaction:

$$CuSO_4 + Fe = FeSO_4 + Cu \qquad (1)$$

Laist and Frick,[3] to determine the copper-precipitating value of sponge iron, used an acidified copper sulfate solution and, after the precipitated copper had been removed by filtration, analyzed the solution for copper by the iodide method. Eastman[4] digested the sample over night in a neutral solution of copper sulfate in an atmosphere of carbon dioxide and determined the copper in the precipitate by the ordinary electrolytic method. Others have used an acid solution and analyzed the precipitate for copper by the iodide method. These methods are suitable for determining the copper-precipitating value if the conditions under which the copper is precipitated are identical with those existing in the plant. They are, however, inaccurate for determining metallic iron unless the acidity of the solution is kept within certain well-defined limits, as will be pointed out in detail later.

The British Pharmacopeia (1905)[5] describes a method using a neutral solution of copper sulfate, determining the iron in the filtrate by precipitating iron hydroxide with ammonium hydroxide, burning, and weighing the Fe_2O_3. This method is open to the objection that it is difficult to burn a large precipitate of iron hydroxide to Fe_2O_3 without some contamination by Fe_3O_4.

(2) The Mercuric Chloride Method—This method is most commonly used for the determination of metallic iron in *ferrum reductum*, and many consider it the standard method. In this method[6] the sample is treated with a neutral solution of mercuric chloride, which dissolves the metallic iron according to Equation 2, and leaves the oxide of iron unattacked.

$$Fe + HgCl_2 = FeCl_2 + Hg \qquad (2)$$

The iron in the filtrate is determined by titrating with either potassium permanganate or potassium dichromate, or by precipitating with ammonium hydroxide, burning, and weighing as Fe_2O_3. To prevent oxidation, the precipitation is carried out in an atmosphere of carbon dioxide. Frerichs[5] describes various modifications of the mercuric chloride method as the standard methods of the German, Swedish,

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[1] Received May 8, 1922. Published by permission of Director of Bureau of Mines.

[2] Metallurgist and Junior Metallurgical Chemist.

[3] "The Precipitation of Copper from Solution at Anaconda," *Trans. Am. Inst. Min. Eng.*, **49** (1914), 694.

[4] Personal communication.

[5] G. Frerichs, "Die Bestimmung des Eisens im Ferrum Reductum (The Determination of Iron in *Ferrum Reductum*)," *Arch. Pharm.*, **246** (1908), 200.

[6] F. P. Treadwell and Wm. T. Hall, "Analytical Chemistry," Vol. 2, "Quantitative Analysis," 4th ed., **1916**, p. 611; A. H. White, "Methods of Metallurgical Analysis," p. 67; U. S. Pharmacopeia, **1916**, p. 172.

Swiss, and Belgian Pharmacopeias for the analysis of *ferrum reductum*, and the U. S. Pharmacopeia for 1916 outlines a similar method. These modifications differ only in the method of dissolving the metallic iron which is determined in the filtrate by the ordinary gravimetric method. The mercuric chloride method is accurate but long, and requires much care in its execution.

(3) THE FERRIC CHLORIDE METHOD[6]—In the ferric chloride method the sample is treated with a solution of ferric chloride which dissolves the metallic iron, forming ferrous chloride, according to the following equation:

$$2FeCl_3 + Fe = 3FeCl_2 \qquad (3)$$

The ferrous iron is titrated with potassium permanganate. The operation is carried out in an atmosphere of carbon dioxide, and twelve hours are recommended for the complete solution of the iron. The method is accurate but long, and much care must be exercised in preventing oxidation of the ferrous chloride.

(4) THE HYDROGEN EVOLUTION METHOD—The hydrogen evolution method[7] consists of dissolving the metallic iron in dilute sulfuric acid, measuring the volume of hydrogen evolved, and calculating the equivalent amount of iron. The method is accurate in the absence of ferric oxide, but requires elaborate apparatus and could not be applied easily where many determinations are required. Furthermore, practically all sponge iron samples contain some iron oxide, which will dissolve in the acid to form a certain amount of ferric sulfate. This ferric sulfate will react upon the metallic iron forming ferrous sulfate, thus dissolving the iron without liberating any hydrogen. Hence, low results are to be expected when using the hydrogen evolution method to determine metallic iron in sponge iron samples that contain appreciable amounts of ferric oxide soluble in sulfuric acid.

(5) THE OXIDATION METHOD—In the oxidation method, the sample is ignited in a current of air until constant weight is obtained. The iron is then supposed to be in the form of Fe_2O_3 and the per cent of metallic iron is calculated from this weight. This method has been used in the analysis of *ferrum reductum*,[8] but is not trustworthy because of the difficulty of oxidizing the iron entirely to Fe_2O_3 and because the weight of another substance present in the sample may change during the heating.

EXPERIMENTAL

All the methods described above were used for determining the metallic iron in sponge iron. The mercuric chloride method proved to be the most accurate, while the copper sulfate method was most easily performed. Concordant values for metallic iron could not be obtained with the copper sulfate method by determining the copper and calculating the equivalent iron. High results were obtained when the copper sulfate solution was neutral, low ones when the copper sulfate solution was slightly acid, and variable ones, which depended upon the content of iron oxide, when the copper sulfate solution was strongly acid. Results that agreed closely with those obtained with the mercuric chloride method were repeatedly obtained by titrating the iron that had been dissolved as ferrous sulfate by the copper sulfate solution.

In order to study the precipitation of copper from copper sulfate solutions by metallic iron, the following experiments were performed:

A sample of U. S. P. *ferrum reductum*—pure metallic iron prepared by reduction of pure Fe_2O_3 with hydrogen—was obtained and its total iron content determined in the usual manner. The average of several determinations, which checked very closely, showed that the total iron content in this material was 97.94 per cent (Table I).

TABLE I
(250-mg. sample used)

No.	$KMnO_4$ Cc.	Iron Per cent
1	49.35	97.91
2	49.35	97.91
3	49.40	98.01
	AVERAGE	97.94

Copper sulfate solutions were prepared by dissolving pure anhydrous copper sulfate in water, filtering, and adding the requisite amounts of water and acid. Several solutions were prepared—one neutral, and the others containing 0.025, 0.05, 0.075, 0.1, 0.2, 0.4, 0.5, 2.0, 6.0, 8.0, and 10.0 per cent of sulfuric acid by volume. These solutions contained about 100 g. of anhydrous copper sulfate per liter, experiments previously made having shown that various concentrations of copper sulfate had no effect upon the results. Samples of the *ferrum reductum* weighing 250 mg. were placed in covered beakers, treated with 30 cc. of one of the various copper sulfate solutions, and boiled for 10 min. The solution was immediately filtered, and the precipitate washed well with hot water. The filtrate was diluted with water to 75 cc., a strip of metallic aluminium and 7 cc. of concentrated sulfuric acid were added, and the solution was boiled until all the copper had been precipitated. The solution was then filtered, cooled, and titrated at once with potassium permanganate and the per cent metallic iron calculated. The first copper precipitate, which was formed by the metallic iron, was dissolved in nitric acid and the copper determined by the ordinary iodide method. The copper that was precipitated by the aluminium was dissolved in nitric acid and likewise determined by the iodide method. In some cases this procedure was modified, and, instead of dissolving the metallic copper that was precipitated by the aluminium, a new sample was treated and the copper was precipitated as cuprous sulfide by boiling with sodium thiosulfate solution, and determined in the usual manner. In this case the direct titration of the iron in the filtrate could not be performed. Therefore, several samples were weighed and treated independently, determining the iron in the filtrate by titration with potassium permanganate. The amount of iron equivalent to the copper that had been precipitated, as shown by analysis of both the filtrate and the precipitate, was calculated on the basis of the equation:

$$CuSO_4 + Fe = FeSO_4 + Cu \qquad (4)$$

Some of the results obtained by titrating the ferrous sulfate are shown in Table II, and the results showing the per cent of metallic iron obtained by titrating the copper are shown in Table III for comparison with each other and with the per cent of metallic iron obtained by titrating the ferrous sulfate. Fig. 1 was plotted from the results in Table III to show the relation between the amount of copper precipitated and the acid concentration. Fig. 2 was plotted using a larger scale for the abscissa in order to show more clearly the relationship in the weaker acid concentrations. From Tables II and III, and Figs. 1 and 2, it will be seen that:

1—The sum of the weights of the copper in the residue and in the filtrate closely approximates the total amount of copper originally contained in the copper sulfate, showing that the copper determinations were accurately performed.

2—The values for the per cent of metallic iron obtained by titration of the ferrous iron in the filtrate checked very closely with each other and with those for the per cent of total iron.

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[7] Henry G. Martin, "Method for the Estimation of Metallic Iron in the Presence of [illegible]," [illegible] 29 (1907), 1211.

[8] [illegible] W. W[illegible], "[illegible] Reductum," J. Chem. Soc. (London), 112 [illegible] Die Bestimmung des Eisens im Ferrum Reductum (The Determination of Iron in Ferrum Reductum)," *Arch. Pharm.*, 255 (1917), 357.

3—In a neutral solution the values for the per cent of metallic iron obtained by titrating the copper in the filtrate or that in the precipitate are higher than the per cent of total iron, and they decrease as the acidity of the copper sulfate solution increases. The decrease is very large until an acid concentration of 0.5 per cent is obtained, after which the decrease is small as the acid concentration increases.

4—When the acidity is 0.075 per cent sulfuric acid, the values obtained by the three operations check, but as the content of sulfuric acid becomes greater than 0.075 per cent, the values for the per cent of metallic iron obtained from the two copper titrations decrease progressively. The acidity of 0.075 per cent does not represent the actual acidity during the entire time of precipitation since the volume of the solution decreased somewhat during boiling, and, therefore, this value is more or less an arbitrary one.

TABLE II—METALLIC IRON OBTAINED BY TITRATION OF FERROUS SULFATE
(250-mg. sample used)

Condition of Solution	$KMnO_4$ Cc.	Iron Per cent
Neutral	49.25	97.71
Neutral	49.30	97.81
Neutral	49 35	97.91
Neutral	49.30	97.81
Neutral	49.50	98.20
Neutral	49.10	98.00
Neutral	49.15	98.10
Neutral	49.00	97.81
Neutral	49.15	98.10
Acid	49.05	97.90
Acid	49 00	97.81
Acid	49.10	98.00
Acid	49.15	98.10
	AVERAGE	97.95

The high results are caused by the precipitation of more copper than corresponds to the equation:

$$CuSO_4 + Fe = Cu + FeSO_4 \qquad (5)$$

Indications are that some cuprous oxide is formed, according to the following equation:

$$2CuSO_4 + Fe + H_2O = Cu_2O + FeSO_4 + H_2SO_4 \qquad (6)$$

and that the presence of acid counteracts the tendency toward this reaction.

The low results are caused by the dissolving in sulfuric acid of some of the iron, forming hydrogen which escapes without precipitating copper.

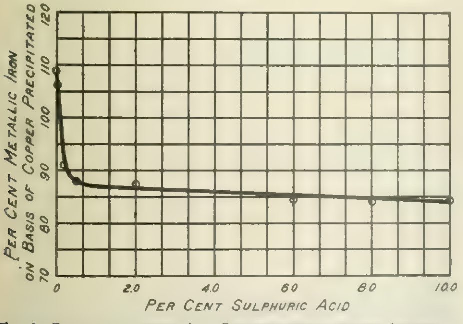

FIG. 1—RELATION BETWEEN ACID CONCENTRATION AND THE AMOUNT OF COPPER PRECIPITATED, ON BASIS OF 97.95 PER CENT METALLIC IRON

Further experiments similar to those described above were performed in which several different samples of sponge iron were substituted for the *ferrum reductum*. These sponge iron samples contained iron oxide, silica, and coke, and the particles were large and in some cases not porous. Results were obtained which bore the same relation to each other as were found when using the purer *ferrum reductum*, except that when the higher acid concentrations were used, some of the iron oxide dissolved and thereby produced high results. The sponge iron dissolved more slowly in the copper sulfate solution than did the *ferrum reductum*, but a 15-min. boiling was sufficient. Prolonged boiling of the neutral solution caused the formation of a brown scum which contained iron and caused low results.

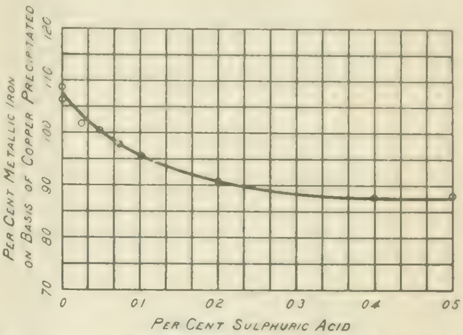

FIG. 2 RELATION BETWEEN ACID CONCENTRATION AND THE AMOUNT OF COPPER PRECIPITATED, ON BASIS OF 97.95 PER CENT METALLIC IRON

TABLE III—COMPARISON OF METALLIC IRON OBTAINED BY TITRATING COPPER AND BY TITRATING IRON

	COPPER						
$CuSO_4$ Solution Per cent H_2SO_4 by Volume	In Residue G.	In Filtrate G.	Total in Residue and Filtrate G.	Total Copper Added as $CuSO_4$ G.	Per cent Metallic on Equiv. to Copper Detd. by Titration of Copper	Average Per cent Metallic Iron by Titration of $FeSO_4$	Average Per cent Total Iron
Neutral	0.3099	0 0714	0.3813	0.3822	108.89	97.95	97.94
Neutral	0.3196	0.0718	0.3824	0.3822	109.14	97.95	97.94
Neutral	0.3029	0.0656	0.3685	0.3687	106.43	97.95	97.94
Neutral	0.3032	0.0653	0.3685	0.3687	106.53	97.95	97.94
0.025	0.2892	0.2699	0 5591	0.5620	101.64	97.95	97.94
0.025	0.2890	0.2685	0.5575	0.5620	101.54	97.95	97.94
0.050	0.2856	0.2764	0.5620	0.5620	100.35	97 95	97.94
0.050	0.2858	0.2743	0.5601	0.5620	100.42	97.95	97.94
0.075	0.2784	0.0889	0.3673	0.3687	97.82	97.95	97.94
0.075	0.2781	0.0892	0.3673	0.3687	97.71	97.95	97.94
0.10	0.2704	0.2878	0.5582	0.5620	95 01	97.95	97.94
0.10	0.2706	0.2892	0.5598	0.5620	95.08	97.95	97.94
0.20	0.2588	0.3010	0.5598	0.5620	90.93	97.95	97.94
0.20	0.2586	0.3032	0.5618	0.5620	90.86	97.95	97.94
0.40	0.2492	0.3121	0.5613	0.5620	87.56	97.95	97.94
0.40	0.2490	0.3126	0.5616	0.5620	87.49	97.95	97.94
0.50	0.2506	0.3092	0.5588	0.5620	88.05	97.95	97.94
0.50	0.2504	0.3104	0.5608	0.5620	87.98	97.95	97.94
2.0	0.2392	...	...		83.98	97.95	97.94
2.0	0.2443	...	...	...	85.77	97.95	97.94
6.0	0.2341	...	...	...	82.19	97.95	97.94
6.0	0.2315	...	...	...	81.28	97.95	97.94
8.0	0.2300	...	...	...	80.75	97.95	97.94
8.0	0 2326	...	...	...	81.66	97.95	97.94
10.0	0.2336	...	...	...	82.01	97.95	97.94
10.0	0.2305	...	...	...	80.92	97.95	97.94

Ferrous sulfide precipitates copper from copper sulfate solution, forming ferrous sulfate. Hence, its presence will give a higher copper precipitating value and a high value for the per cent metallic iron. Usually, not all of the iron sulfide reacts and, since only small amounts of it are ordinarily met with, a large error does not result. High results are caused by ferrous sulfide in all of the five methods discussed above.

ANALYTICAL PROCEDURE

After conducting several sets of determinations, the following procedure was adopted and has been used successfully in routine analytical work:

The sample should preferably be crushed to pass a 60-mesh or finer screen. Weigh 500 to 250 mg., depending upon the metallic iron content, into a 400-cc. beaker. Add 15 to 20 cc. of a copper sulfate solution containing about 100 g. per liter. The copper sulfate solution should be free from iron and, if not, a correction must be made for its iron content. Dilute with about 35 cc. of hot water and boil for 15 min., keeping the beaker covered and maintaining a volume of approximately 50 cc. by frequent additions of water. Filter *immediately* into a 250-cc. beaker and wash the residue several times with hot water. Dilute the filtrate to 75 or 100 cc. and add 7 cc. of concentrated sulfuric acid and a sheet of aluminium. Boil until all the copper has been precipitated. Cool rapidly with the aluminium strip in the solution, keeping the beaker covered. Filter into the original beaker, wash well with cold water, dilute to 350 cc. with cold water and titrate *at once* to a pink color with a standard solution of potassium permanganate. Calculate the per cent of iron. This represents the amount of metallic iron in the sample. In this titration the potassium permanganate may be replaced by potassium dichromate, using potassium ferricyanide as an external indicator.

This method has been found reliable in the routine analysis of a large number of sponge iron samples whose metallic iron content varied from 0.5 to 90 per cent.

Some New Sensitizers for the Deep Red[1,2]

By **C. E. K. Mees** and **G. Gutekunst**

RESEARCH LABORATORY, EASTMAN KODAK CO., ROCHESTER, N. Y

IN THE course of work extending over a number of years, many new dyes derived from quinoline have been prepared and tested for their sensitizing power. A number of compounds prepared in the course of this investigation have been described in a paper by G. Gutekunst and H. LeB. Gray on "The 6-Alkyloxyquinaldines."[3] The purpose of the present paper is to describe three of the new sensitizers that have been selected as having interesting properties, two of which it is proposed to place upon the market.

NAPHTHACYANOLE
(1,1′-DIETHYL-DI-β-NAPHTHOCARBOCYANINE NITRATE)

This dye was prepared as follows:

A solution of 5 g. of β-naphthoquinaldine ethiodide and 5 g. of quinoline ethiodide in .500 cc. of boiling ethanol (95 per cent) was treated with a mixture of 4 cc. formaldehyde (40 per cent) and 60 cc. of 10 per cent alcoholic potash. The dye separated out in the form of little green needles, which on account of their insolubility were converted into the nitrate. This was accomplished by suspending a small amount of the dye in glacial acetic acid (75 cc.) and adding 200 cc. of 1 per cent nitric acid, allowing the mixture to digest for a time (1/2 hr.), and then filtering off the undissolved crystals. The solution was shaken thoroughly with 1 cc. of 10 per cent silver nitrate and the silver iodide filtered off. The dye was precipitated immediately with ammonium hydroxide and recrystallized from methanol.

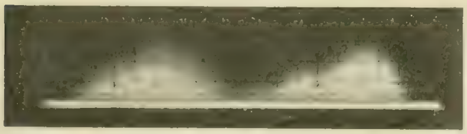

FIG. 1—β NAPHTHACYANOLE

This dye sensitizes powerfully, both when added to the emulsion and when used for bathing ready prepared plates. A spectrum shown in Fig. 1 shows a strong maximum in the deep red at 690$\mu\mu$, and a sensitizing power for the green appreciably less than that shown by pinacyanole. The dye keeps well and is quite suitable for use in the place of pinacyanole where the extreme red sensitiveness is an advantage.

ACETAMINOCYANOLE
(1,1′-DIETHYL-6,6′-DIACETAMINOCARBOCYANINE IODIDE)

This dye was prepared as follows:

A solution of 5 g. 6-acetaminoquinaldine ethiodide and 5 g. quinoline ethiodide in 200 cc. of boiling ethanol was treated with a mixture of 20 cc. of sodium ethylate (1 g. sodium in 50 cc. absolute ethanol) and 5 cc. of formaldehyde. A blue-green solution was formed and green crystals separated on cooling. These were recrystallized from methanol.

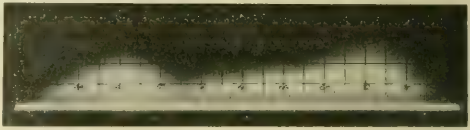

FIG. 2—ACETAMINOCYANOLE IN EMULSION

The dye obtained was found to sensitize powerfully when added to an emulsion, giving a maximum at 730$\mu\mu$. Its spectrum is shown in Fig. 2. When an attempt was made to use this dye in water solution for bathing plates, a very curious result was obtained, the spectrum obtained being that shown in Fig. 3 and corresponding obviously to an entirely different dye. Moreover, it was found that in the preparation of the dye it was necessary to be careful to keep the water content to a minimum, as otherwise the dye had not the characteristic sensitizing maximum at 730$\mu\mu$ but gave a result similar to that obtained when bathing plates in water solution. The probable explanation of these anomalies is that the dye is hydrolyzed by water, the acetyl radical being hydrolyzed off. While the dye, therefore, has some value when used for emulsions, since the plates prepared appear to keep their characteristic properties, it is not thought that it will be of general value, owing to its instability.

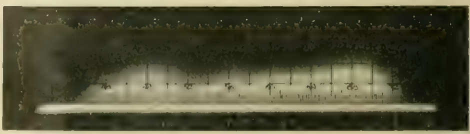

FIG. 3—ACETAMINOCYANOLE BATHED PLATE

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[1] Received J[illegible]

[2] Communication No. [illegible] from the Research Laboratory of the Eastman Kodak Co., Rochester, N. Y.

[3] J. Am. Chem. Soc., 44 (1922), 1741.

A compound is described by Mills and Pope[4] which was prepared by the condensation of 6-acetaminoquinaldine ethiodide and quinoline ethiodide with formaldehyde and alkali and crystallizes in minute green needles. It sensitizes at 6300 to 6800 and more weakly at 5200 to 6300, and thus appears to be an entirely different compound from that described here.

KRYPTOCYANINE

This dye was prepared by the condensation of lepidine ethiodide.[5] On recrystallizing from chloroform, small bronze crystals are obtained. On trial this proved to be the most remarkable sensitizer yet discovered. A great deal of time was expended in purifying it to prevent a fogging action on the emulsion, since when tested in the usual concentration, 1 in 25,000, it gave severe fog, though sensitizing with great power with a maximum at $760\mu\mu$. It was found, however, that the dye was being used in far too great a concentration, and by the use of only $^1/_{20}$ the amount required for pinacyanole excellent results were obtained. The spectrum is shown in Fig. 4. For bathing solutions a concentration of 1 in 500,000 is recommended. The addition of either ammonia or alcohol was found to be a disadvantage.

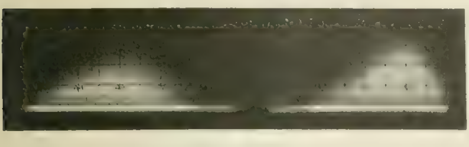

FIG. 4—KRYPTOCYANINE

Tests were made for the extension of the spectrum with kryptocyanine into the extreme infra red. It was found that although its maximum is at a considerably longer wave length than that given by dicyanine, and although up to $850\mu\mu$ its sensitizing power is greater than that of dicyanine, yet beyond this point dicyanine shows a greater sensitizing power, and above $900\mu\mu$ kryptocyanine is almost useless, while dicyanine, employed according to the directions given by Dr. Meggers, is still effective. Nevertheless, kryptocyanine represents a very great advance in the preparation of photographic materials sensitive to the extreme red. Since it confers no green sensitiveness and, indeed, the materials sensitized with it have very little sensitiveness below $680\mu\mu$, infra red effects in ordinary photography can be obtained by the use of a strong yellow filter only, and, employed in this way, it is possible to give very short exposures, one second at $^f/_8$ being quite satisfactory in bright sunlight. The results obtained are those characteristic of photography in the infra red, blue skies appearing dark and green foliage very bright, so that a tree covered with spring leaves appears as if in blossom and the grass on the ground as if it were snow.

It is probable that the dye will have applications in astronomy. At the present time, stars are classified by their color index, this being the relation of the photographic magnitude determined in the violet to the photo visual magnitude determined in the yellow-green, and determination of the extreme red magnitude at $770\mu\mu$ by the use of kryptocyanine will probably extend the value of such studies. Undoubtedly numerous other applications will be found for this dye.

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[4] *Phot. J.*, **40** (1920), 253.

[5] E. Q. Adams and H. L. Haller, *J. Am. Chem. Soc.*, **42** (1920), 2661.

Sources of Moving Picture Films

A large number of films produced and distributed by the United States Department of Agriculture are described in *Department Circular* **233**, which may be obtained from the Superintendent of Documents at a cost of 5 cents a copy. These films are intended primarily for the use of extension and field workers of the department and of officially coöperating institutions, but others may make special arrangements to borrow or to buy copies.

The Publicity Bureau of E. I. du Pont de Nemours & Co., Inc., has at its disposal moving pictures of the war plants, now dismantled, which may be of interest to engineering societies and technical schools. The films, which are all short, are as follows:

Old Hickory, Smokeless Powder
Hopewell, Va., Guncotton Plant
Penniman, Va., Shell-loading Plant
Carney's Point, N. J., Smokeless Powder

A film of the du Pont Dye Works at Deepwater Point, N. J., is also available. No charge is made for the use of these films.

The Industrial Department of the Young Men's Christian Association, 347 Madison Ave., New York, N. Y., is acting as the distributor of industrial and educational moving picture films for the companies listed below. Information in regard to the films may be obtained from the Association.

Air Reduction Co.
All America Cables, Inc.
Alpha Portland Cement Co.
American Multigraph Sales Co.
American Rolling Mill Co.
American Sugar Refining Co.
American University of Beirut
Amoskeag Mfg. Co.
Armour & Co.
Armstrong Cork Co.
Associated Mfrs. of Pipe & Boiler Coverings
Atkins, E. C., & Co.
Auto Strop Safety Razor Co.
Ball Brothers Glass Co.
Barrett Co.
Beech-Nut Packing Co.
Blumenthal, Sidney, & Co., Inc.
Boston Montana Co.
California Fruit Growers' Exchange
Calumet Baking Powder Co.
Carnation Milk Products Co.
Certain-teed Products Corp.
Chicago Railway Equipment Co.
Cleveland & Buffalo Transit Co.
Cleveland Tractor Co.
Cleveland Twist Drill Co.
Colgate & Co.
Commonwealth Steel Co.
Corn Products Refining Co.
Dentinol & Pyorrhocide Co.
Disston, Henry, & Sons
Durham Hosiery Mills
Eisemann Magneto Corp.
Eisner, Sigmund Co.
Elliott Co.
Fruit Despatch Co.
Girl Scouts of America
Graton & Knight Mfg. Co.
Greist Mfg. Co.
Hoover Suction Sweeper Co.
Howard, J. W. & A. P., Co.
International Harvester Co.
International Mercantile Marine Co.
International Silver Co.
Kirkman & Sons
Koehring Machine Co.
Kresge, S. S., Co.
Lamson Company
Long Bell Lumber Co.
Mint Products Co.
Mosler Safe Co.
National Automatic Sprinkler Assn.
National Biscuit Co.
National Carbon Co.
National Coffee Roasters Assn.
National Electric Light Assn.
National Lead Co.
National Life Preserver Co.
National Terra Cotta Society
North East Electric Co.
Northwestern Chemical Co.
Otis Elevator Co.
Plymouth Cordage Co.
Port of New York Authority
Postum Cereal Co.
Prest-O-Lite Co., Inc.
Price, E. V., & Co.
Robert College of Constantinople
Schieren, Chas. A., Co.
Scott Paper Co.
Shredded Wheat Co.
Sinclair Oil Co.
Skinner, Wm., & Sons
Southern Lumber Co.
Stafford, S. S., Inc.
Standard Oil Co.
Standard Pneumatic Action Co.
Stevenson, E. A., & Co., Inc.
Stone & Webster
Swift & Co.
U. S. Cast Iron Pipe & Foundry Co.
Wayne Oil Tank & Pump Co.
Welch Grape Juice Co.
Western Electric Co.
Westinghouse Electric & Mfg. Co.
Wilkes-Barre, Pa., Chamber of Commerce
Winchester R. A. Co.
Women's College of Constantinople
Wood, J. R., & Sons
Wright, E. T., Shoe Co.
Yawman & Erbe Mfg. Co.

Condensation of Vapor from Mixtures of Vapors and Noncondensable Gas[1]

By Barnett F. Dodge[2]

Lewis Recovery Corporation, Cambridge, Mass.

The theory of the condensation of mixtures of vapors and noncondensable gas has been developed in such a way as to enable approximate calculations to be made of the amount of condensate obtainable under given conditions. So far, the theory can only be applied to mixtures of vapors which roughly obey Raoult's law when they exist as liquids. For such mixtures the equations have been developed for both "differential" and "simple" condensation, and it is shown that the two quite different mathematical expressions give nearly identical results for amount of condensate. The equations for "simple" condensation are extended to include mixtures of three or more vapors and noncondensable gas. Several illustrations of the practical applications of the equations are given.

PROCESSES for the recovery of solvents used in industry, for the extraction of gasoline from natural gas, and for the extraction of light oil from coke-oven gas and allied processes, are all primarily concerned with the condensation of vapors from mixtures of these vapors and noncondensable gas. One of the main questions that arises, especially in connection with the design of apparatus for new plants, modification of present processes, and development of new ones, is: How much of the given vapor or mixture of vapors, say gasoline, will be condensed under any given conditions of temperature, pressure, and concentration? It becomes important, then, to have available methods of estimating the amount of recovery or of extraction under given conditions. It is the purpose of this article to develop equations which will enable this quantity to be calculated for certain types of vapors. These equations will be developed in as general a form as possible consistent with simplicity, so that the desired result can be obtained directly by merely substituting proper values of total pressure, vapor pressures of pure liquid components and concentrations.

SINGLE VAPOR COMPONENT

The calculation of the amount of vapor which will condense out of a mixture of a single vapor[3] and noncondensable gas under given conditions of concentration, temperature, and pressure, is relatively simple. For example, the following equation[4] may be used to calculate the per cent of the vapor that will condense:

$$\text{Per cent condensation} \quad \frac{\dfrac{V}{100-V} - \dfrac{p}{D-p}}{\dfrac{V}{100-V}} \times 100 \qquad (1)$$

where V = Volume per cent of vapor in the initial mixture
p = Vapor pressure of the liquid condensate at the final temperature of the system
D = Final total pressure on the system

This same relation may be expressed in a number of ways but Equation 1 expresses it in a general way so that it may be applied directly to a wide variety of conditions.

The following example illustrates the use of this equation:

> Assume that we have air containing 2.0 per cent by volume of benzene vapor and that we wish to know how much of the benzene can be condensed by compressing the mixture to a pressure of 150 lbs. per sq. in. gage and cooling the compressed mixture under constant pressure to 20° C.
>
> From vapor pressure tables we find that p at 20° C. = 75 mm. From the conditions of the problem, we see that
>
> $$V = 2.0, \text{ and } P = \frac{150 + 14.7}{14.7} \times 760 = 8500 \text{ mm.}$$
>
> Substituting in Equation 1 we obtain 56.5 per cent condensed. A similar calculation may be used for condensation of any single vapor by any condition of compression or refrigeration.

Space does not permit the citing of the many practical applications of this equation. It is hoped that this phase of the subject can be taken in detail in a second paper. The curves shown in Fig. 1 are given, however, to show in a general way how the equation may be applied to the study of a solvent recovery problem. These curves, which were constructed from calculations made by the aid of the equation, enable one to predict immediately what percentage recovery would be obtained by cooling different gasoline-air mixtures (gasoline was equivalent to hexane in vapor pressure) to certain given temperatures at a pressure of one atmosphere. For example, by reference to the figure it can be seen that a 15 per cent concentration by volume just begins to condense at 20° C., is one-half condensed at 4° C., and over 90 per cent condensed at −30° C. On the other hand, a 5 per cent concentration does not begin to condense until cooled to −4° C. Such information, which may be closely checked in practice, is a valuable guide in the determination of the best process to use in the recovery of a given solvent under given conditions.

TWO VAPOR COMPONENTS

The usual problem that arises in practice involves the treatment of gases containing, not a single vapor component, but a mixture of two or more vapors. Such a problem is usually handled by assuming some sort of an average vapor with properties that represent some kind of a weighted average of the properties of the single pure components. It is our object in the following discussion to develop the theory of the condensation of complex mixtures and incidentally to show whether or not the use of an average is justified.

As far as could be ascertained from a brief study of the literature, the condensation of mixtures of vapors in a noncondensable gas has not been treated from a theoretical standpoint to develop equations of practical use. The theory of the condensation of binary mixtures not containing a noncondensable gas has been developed, but the resulting equations cannot be conveniently applied to this case, as will be shown later.

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[1] Received April 4, 1922.

[2] Lecturer in Chemical Engineering, Harvard University.

[3] By the term "vapor" we mean a gas which is relatively near its boiling point.

[4] The derivation of this equation is very simple. Assuming that the vapor and the noncondensable gas mixed with it obey the simple gas laws, then $\frac{V}{100-V}$ = mols of vapor per mol of noncondensable gas in the initial mixture. Assuming that the final gas mixture comes to equilibrium with the condensed liquid at the final gas temperature in the system, which is almost always the case, then $\frac{p}{D-p}$ = mols of vapor per mol of noncondensable gas in the final mixture (*i. e.*, since p is the vapor pressure of the condensate, it must also be the partial pressure of the vapor remaining in the gas, regardless of the total pressure on the system). Since the noncondensable gas remains constant throughout, the mols of vapor per mol of noncondensable at the start minus the same ratio at the end divided by the ratio at the start gives the fraction condensed.

It is obvious that the liquid which condenses from a mixture of vapors will not have the same composition as the initial vapor, and that the composition will vary throughout the process.

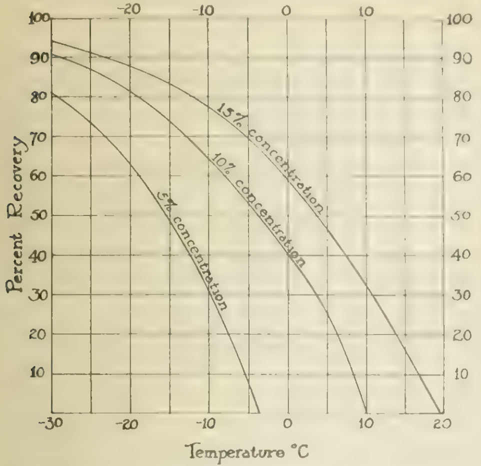

FIG. 1—PER CENT CONDENSATION AS A FUNCTION OF FINAL TEMPERATURE FOR THREE DIFFERENT CONCENTRATIONS OF HEXANE AT ATMOSPHERIC PRESSURE

Consequently, it will be necessary, in deriving a formula for per cent condensation, to have a relation between liquid composition and vapor composition at equilibrium for the components under consideration. Raoult's law expresses this relation exactly for ideal solutions and approximately for a great many solutions, in which the components are somewhat related. For example, such binary mixtures as benzene and toluene, hexane and heptane, methanol and ethanol, and many others, obey Raoult's law very closely. In the discussion that follows it will be assumed that we are interested only in mixtures that obey Raoult's law at least approximately.[5] For mixtures not obeying Raoult's law the vapor pressure relations are more complex and such mixtures will be considered beyond the scope of this paper.

Before developing the theory, it is necessary to recognize that a condensation may take place in two ways.[6] These two ways are limiting ones in that all condensations in practice are intermediate between the two, but approach one or other of the limiting types. Let us consider a condensation to be composed of a series of very small steps, each yielding a very small increment of condensate between given temperature limits. If we allow all these successive increments of condensate to mix and remain in contact with the residual gas, then we have a *simple* condensation. The distinguishing characteristic of *simple* condensation is, then, that at any instant in the process the residual vapor is in equilibrium with the total amount of liquid originally associated with it. If, on the other hand, we keep the small increments of condensate separate during the process, then at any instant the residual vapor will be in equilibrium only with the last increment of condensate, and the condensation may be said to be a *differential one.* Neither of these limiting types is exactly realized in practice but the common cases approach one or the other type. For instance, if a mixture of noncondensable gas and vapor were slowly cooled in a receiver and no condensate removed during the process, the condensation would be practically *simple*. If, on the other hand, the condensate were removed as fast as formed, the condensation would be practically *differential.* A *differential* condensation is probably quite closely realized when the vapor from a mixture containing noncondensable gas is being continuously condensed in a surface condenser, particularly if the condensate is drawn off at a number of points to minimize mixing.

In the ordinary condensation of binary mixtures in connection with distillation, these two methods of condensation lead to quite different results, but it will be shown later that, as far as the *amount* of condensate obtained from the condensation of vapors from mixtures containing noncondensable gas is concerned, the results are practically the same. This is a fortunate fact as it greatly simplifies the mathematical treatment.

We will now proceed to develop the theory for both types of condensation, in order to prove this point and obtain equations which can be applied to the solution of problems.

SIMPLE CONDENSATION—In developing equations for simple condensation, the following nomenclature will be used:

x = mol fraction of a component in the *gas* phase.
y = mol fraction of a component in the *liquid* phase.
The prime mark (′) and double prime (″) will represent initial and final states, respectively.
D = total pressure, which is a constant in any given condensation.
p = vapor pressure of a pure liquid component at the final temperature in the process.
Subscripts a, b, c, etc., will refer to the components.
W = number of mols of condensate.
Thus y_a'' would represent a mol fraction of component "A" in the liquid in the final condition.

Taking *one mol* of initial gas as the basis for all calculations, we may establish the following condition equations for the case of two vapors mixed with noncondensable gas from Raoult's law and that of conservation of mass:

$$x_a'' \mathrm{D} = y_a'' p_a \qquad (2)$$

$$x_b'' \mathrm{D} = y_b'' p_b \qquad (3)$$

$$x_a' - x_a''(1 - \mathrm{W}) = y_a'' \mathrm{W} \qquad (4)$$

$$x_b' - x_b''(1 - \mathrm{W}) = y_b'' \mathrm{W} \qquad (5)$$

$$y_a'' + y_b'' = 1 \qquad (6)$$

Equations 2 and 3 state that for each component the partial pressure of that component in the final vapor equals the vapor pressure of the same component over the final condensate. In other words, we are equating the partial pressure given by Dalton's law to the vapor pressure given by Raoult's law. Equations 4 and 5 state that the amount of a given component condensed from the gas equals the amount of the same component appearing in the liquid. Equation 6 states that the sum of the mol fractions of all the components in the liquid equals unity.

There are five unknowns, the four final mol fractions and W, the amount condensed, and there are five equations; therefore, we can solve for W. Omitting intermediate steps, we obtain:

$$\frac{x_a'}{\mathrm{W}\left(1 - \frac{p_a}{\mathrm{D}}\right) + \frac{p_a}{\mathrm{D}}} + \frac{x_b'}{\mathrm{W}\left(1 - \frac{p_b}{\mathrm{D}}\right) + \frac{p_b}{\mathrm{D}}} = 1 \qquad (7)$$

For the sake of abbreviation, let

$$\frac{p_a}{\mathrm{D}} = \alpha_1, \quad \frac{p_b}{\mathrm{D}} = \alpha_2, \; 1 - \alpha_1 = k_1, \text{ and } 1 - \alpha_2 = k_2.$$

The Equation 7 becomes:

$$\frac{x_a'}{k_1 \mathrm{W} + \alpha_1} + \frac{x_b'}{k_2 \mathrm{W} + \alpha_2} = 1 \qquad (8)$$

By noting that Equation 8 is a quadratic of the form $\mathrm{AW}^2 + \mathrm{BW} + \mathrm{C} = 0$, where

$$\mathrm{A} = -k_1 k_2$$

$$\mathrm{B} = x'_a k_2 + x_b' k_1 - \alpha_1 k_2 - \alpha_2 k_1$$

$$\mathrm{C} = x'_a \alpha_2 + x_b' \alpha_1 - \alpha_1 \alpha_2$$

we can solve directly for W the amount of condensate.

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[5] It should be noted, in this connection, that some mixtures apparently deviate widely from Raoult's law when the normal molecular weights are used, but approximately obey the law when a fictitious molecular weight is used for one of the components. The equations to be developed apply to such mixtures.

[6] W. K. Lewis, THIS JOURNAL, **1** (1909), 522; Alcan Hirsch, *Ibid.*, **2** (1910), 409.

$$\text{Thus } W = \frac{-B \pm \sqrt{B^2 - 4AC}}{2A} \tag{9}$$

For any given set of conditions, A, B, and C may be determined and W obtained. W will equal the mols condensed per mol of original gas. If M_a and M_b are the molecular weights of components A and B, respectively, then the lbs. condensed per mol of gas will equal (y_a'' W M_a + y_b'' W M_b). This can readily be determined after W has been calculated.

Before applying this equation, we will next derive the analogous equation for differential condensation, after which we will compare the two on definite numerical problems.

Differential Condensation—We may again write the conditions for equilibrium, namely, the equality of partial pressure of a component in the vapor and the vapor pressure of the same component over the liquid, omitting the primes to indicate any instant.

$$\text{Thus,} \quad x_a D = y_a P_a \tag{10}$$

$$\text{and} \quad x_b D = y_b P_b \tag{11}$$

It is more convenient for our purpose to express the mol fractions as a ratio of number of mols of each component to a total number of mols. Thus, if n = number of mols of a component in the gas, m = number of mols of a component in the liquid, N = total mols of gas, and M = total mols of liquid, then Equations 10 and 11 become:

$$\frac{n_a D}{N} = \frac{m_a P_a}{M} \tag{12}$$

$$\text{and} \quad \frac{n_b D}{N} = \frac{m_b P_b}{M} \tag{13}$$

$$\text{Dividing (12) by (13) we obtain} \quad \frac{n_a}{n_b} = \frac{P_a}{P_b} \times \frac{m_a}{m_b} \tag{14}$$

If only a differential amount of liquid is to be in equilibrium with the gas at any point according to our definition of differential condensation, then we can replace m_a and m_b by dm_a and dm_b, which are obviously equal to dn_a and dn_b, respectively.

There results:

$$\frac{n_a}{n_b} = \frac{P_a}{P_b} \cdot \frac{dn_a}{dn_b} \tag{15}$$

$$\text{or} \quad \int \frac{P_a}{P_b} \cdot \frac{dn_a}{n_a} = \int \frac{dn_b}{n_b} \tag{16[7]}$$

To integrate this equation, we may assume that P_a/P_b is a constant, c. This is only an approximation as c varies with the temperature throughout the condenser, but the variation in c is not great if the temperature range is narrow. It can also be shown that considerable variation in c affects the final result but slightly.

The integral of this equation is obviously

$$c \log n_a = \log n_b + K \tag{17}$$

where K is a constant involving initial and final conditions.

For the purpose of calculating W, the amount condensed, it is simpler to integrate between limits. The upper limits are n_a' and n_b', respectively, and the lower limits, n_a'' and n_b'', will involve W. Consequently, we will obtain equations relating W with other variables which will be known for any specific problem and we can at once solve for W.

n_a'' and n_b'', the number of mols of the two condensable components in the gas at the end of the condensation, are not directly known but can be expressed in terms of the initial number of mols, and W, and certain known constants. The final equations are given as follows:

$$n_a'' = \frac{p_a(1 - W) + cD(W - n_a' - n_b')}{D(1 - c)} \tag{18}$$

$$\text{and} \quad n_b'' = \frac{D(n_a' + n_b' - W) - p_a(1 - W)}{D(1 - c)} \tag{19}$$

These two equations are based on *1 mol* of *initial gas*. Substituting these limits in the integrated form of the equation, we obtain as a final equation for differential condensation,

$$c \log \left[\frac{n_a' D(1 - c)}{p_a(1 - W) + cD(W - n_a' - n_b')}\right] = \log \left[\frac{n_b'(1 - c)D}{D(n_a' + n_b' - W) - p_a(1 - W)}\right] \tag{20}$$

This equation contains a relation between the amount condensed during a differential condensation and the final temperature in the condenser, given the initial concentration and the total pressure. The temperature does not appear as such in the equation, but is involved in p_a, the vapor pressure of pure A at the final temperature. The relation is not a direct one, but the equation may be solved readily by trial and error, and it is just as well to leave it in the above form. The method of solution is fairly simple, usually involving only a few trials.

Application of the Equations for Two Components—We have now two equations for calculating W, one for simple condensation and one for differential condensation. The former is much the simpler and easier to use, and it happens that the two give practically the same result for W over quite wide limits, so that the simpler one can generally be used for both cases.[8] The best way to show this is to take a number of cases and actually use both equations and compare the results. The following table shows the results of several calculations:

Case	Per cent Condensed by Weight[1] Simple Condensation	 Differential Condensation	Mol Per cent of A[2] in the Residual Vapor Simple Condensation	 Differential Condensation
3 per cent benzene and 1 per cent toluene compressed to 5160 mm. (100 lbs./sq. in. abs.) and cooled at constant press to 20° C.[3]....	71.8	68.7	87.5	94.5
20 per cent benzene and 10 per cent toluene cooled to 20° C. at 760 mm.	81.6	76.6	87.0	95.0
3 per cent benzene and 1 per cent toluene compressed to 35 lbs./sq. in. abs. and cooled to 20° C.	28.2	27.5	...	....
15 per cent methanol and 5 per cent ethanol cooled to 0° C. at 760 mm	88.0	86.0	....	....

[1] Per cent figure based on *vapor* alone without the noncondensable gas.
[2] A refers to the more volatile component.
[3] Per cent by volume in mixtures with air or other noncondensable gas.

It is quite evident that the two equations give practically the same result as far as weight of condensate is concerned, for a

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[7] The equation given by Lewis[5] for condensation of distilled liquids is, when expressed in the above nomenclature:

$$\int \frac{dW}{W} = \int \frac{dx}{y - x}$$

When dealing with a binary mixture of two condensable components with no noncondensable gas present, this equation can be solved by expressing y as a function of x and integrating, either by straight mathematical processes or by a graphical method. In the case of the condensation of vapors from mixtures containing noncondensable gas, y is not only a function of x, but also of W, if x is based on the total gas, condensable plus noncondensable. The di[illegible] obtained by expressing y as a function of x and W is not readily solved by ordinary methods. On the other hand, if x is based on the condensable gas only, then y is a definite function of x only, but in that case the total pressure, which as will appear later, enters into the constant of integration, must also be the total pressure on the *condensable* components only, and hence will not be constant. Consequently, we were led to develop the equation in another form suggested by a similar equation for distillation in Young's "Fractional Distillation."

[8] It should be noted that the two equations also apply to the case of binary vapor mixtures containing no noncondensable gas, but it is by no means true that the two different equations lead to even approximately the same amount condensed in many cases.

wide variety of conditions. As would be expected, the differential condensation leaves a residual vapor considerably richer in the more volatile component than does simple condensation.

The mol per cent of A in the residual vapor is

$$\frac{n_a''}{n_a'' + n_b''} \times 100$$

For differential condensation, n_a'' is given by Equation 18 and n_b'' is given by Equation 19. For simple condensation we can obtain x_a'' by combining Equations 2 and 4, giving:

$$x_a'' = \frac{x_a' \, p_a}{\text{W} \, (\text{D} - p_a) + p_a}$$

and then $n_a'' = x_a'' \, (1 - \text{W})$

These equations were used to obtain the mol per cent of A in the residual vapor, figures for which are given in the table.

Let us now consider more in detail the application of the equations to some more numerical problems. Having shown that the two different equations are identical for most practical purposes as far as the *amount* of condensate is concerned, we may use only the simpler one. Assume that we had a mixture of benzene and toluene vapor in air at 1 atm., containing 3 per cent benzene and 1 per cent toluene by volume, and wished to know how much, if any, would condense at 20° C. In the first place, it is obvious that $x = \frac{\text{V}}{100}$, where V = volume per cent of the gas in question. From vapor pressure tables we find that $p_a = 75$ mm. and $p_b = 22$ mm. Then $\alpha_1 = \frac{75}{760} = 0.0986$ and $\alpha_2 = \frac{22}{760} = 0.029$; $k_1 = 0.9014$ and $k_2 = 0.971$. From these values we may solve for A, B, and C, to be used in Equation 9.

Thus we find that: $\text{A} = -0.875$; $\text{B} = -0.0838$; $\text{C} = -0.001$.

Substituting in Equation 9 we find that both roots are negative. In other words, nothing will condense from this mixture under these conditions. Furthermore if C = O in Equation 9, W = O is one root and the other is negative. That is, if C = O, the mixture is just at the saturation point. Equating C to O, we see that:

$$x_a' \, \alpha_2 + x_b' \, \alpha_1 = \alpha_1 \, \alpha_2$$

or

$$x_a' \, p_b + x_b' \, p_a = \frac{p_a \, p_b}{\text{D}} \qquad (21)$$

Equation 21 may be used as a criterion to tell whether a given mixture will or will not deposit any liquid. If

$$x_a' \, p_b + x_b' \, p_a < \frac{p_a \, p_b}{\text{D}}$$

it is obvious that the mixture is below the condensation point, and conversely if

$$x_a' \, p_b + x_b' \, p_a > \frac{p_a \, p_a}{\text{D}}$$

then condensation will take place. These expressions are useful for predicting qualitatively whether or not any condensation will take place under given conditions. For example, assume that we wish to know if the same mixture given above will condense any liquid when compressed to 100 lbs. per sq. in. gage pressure and cooled then to 20° C. In this case

$$\text{D} = \frac{114.7}{14.7} \times 760 = 5940 \text{ mm.}$$

Now $x_a' \, p_b + x_b' \, p_a = 1.98$ for these conditions and $\frac{p_a p_b}{\text{D}} = 0.252$

Then, according to the criterion established above, condensation will take place. Furthermore, we may readily calculate at what pressure condensation will start at any given temperature. Thus, by rearranging Equation 21, we find that

$$\text{D} = \frac{p_a \, p_b}{x_a' \, p_b + x_b' \, p_a} \qquad (22)$$

Applying this to the same conditions of temperature and concentration of benzene and toluene, we find that D = 1170 mm = 22.7 lbs. per sq. in. abs.

At this point we can advantageously make another comparison of the two equations for the different types of condensation. If we let W = O in Equation 20, we obtain

$$c \log \left[\frac{n_a' \, \text{D} \, (1 - c)}{p_a - c \, \text{D} \, (n_a' + n_b')}\right] = \log \left[\frac{n_b' \, \text{D} \, (1 - c)}{(n_b' + n_b') \, \text{D} - p_a}\right] \qquad (23)$$

From this equation we should be able to calculate the pressure to give initial condensation with any given mixture at a given temperature. Furthermore, this equation should give exactly the same initial condensation point as Equation 22. One may easily prove this by substituting the value of D given by Equation 22 in Equation 23. We then obtain $c \log 1.0 = \log 1.0$, thus satisfying the equation exactly. Therefore, the two equations do predict the same initial condensation point.

Mixtures of More than Two Components

For the case of simple condensation it is fairly easy to develop equations for the calculation of weight condensed for any number of components, provided Raoult's law is approximately obeyed. For example, for the case of three components we can establish the following condition equations, exactly analogous to Equations 2 to 6, inclusive:

$x_a'' \, \text{D} = y_a'' \, p_a$, and two similar equations with subscripts *b* and *c*, $x_a' - x_a'' \, (1 - \text{W}) = y_a'' \, \text{W}$, and two similar equations with subscripts *b* and *c*; $y_a'' + y_b'' + y_c'' = 1$.

We have seven equations and seven unknowns, and consequently we can solve the equations simultaneously. The solution is as follows, using the same abbreviations as before:

$$\frac{x_a'}{k_1 \, \text{W} + \alpha_1} + \frac{x_b'}{k_2 \, \text{W} + \alpha_2} + \frac{x_c'}{k_3 \, \text{W} + \alpha_3} = 1 \qquad (24)$$

This is a cubic equation in W and is readily solved by trial and error. It is simpler to leave it in the form given than to clear of fractions. Furthermore, the equation for any number of components can readily be deduced in this form by simply adding on more terms of a symmetrical type. For example, for four components the left-hand number contains an additional term.

$\frac{x'_d}{k_4 \, \text{W} + \alpha_4}$ and the right-hand number is always 1.0

The analogous equations for differential condensation we will not give here, though they can be developed just as readily as the ones for binary mixtures. It will be assumed, from analogy to the binary case, that the two will give practically the same results for *amount* of condensate.

Application of Equations for Three Components

The equations for more than two components could undoubtedly be applied to the quantitative study of the phenomena that take place in the condensation of gasoline-air mixtures, but unfortunately we have no simple way of ascertaining the composition of the gasoline. It is quite likely that the several different hydrocarbons in gasolines would form a mixture obeying Raoult's law fairly well. We can, however, make use of the equations to explain certain phenomena that do arise in practice. For instance, in processes for gasoline recovery from air-gasoline or inert gas-gasoline mixtures, it is customary to assume an average molecular weight and then an average vapor pressure for the gasoline as a basis for making calculations for design and other purposes. Where the recovery process consists of a series of condensations at different pressures, this procedure usually gives about the correct result for the first condensation, but almost always gives much too high a result for the succeeding ones. In other words, the total yield is generally considerably less than would be predicted by the average vapor pressure method. By choosing a hypothetical case and applying the equations developed, we can easily show that this is to be expected. Assuming a gas containing 3 per cent pentane, 6 per cent hexane, 2.5 per cent heptane, 1.0 per cent octane, and the rest air (per cents by volume), the equation predicts that 48 per cent of the total solvent will be condensed at 20° C. and 30 lbs. per sq. in. abs. The average molecular weight method predicts a condensation of 46 per cent and thus checks the equation. The residual vapor will now contain about 2.4 per cent pentane, 3.3 per cent hexane, 0.66 per cent heptane, and 0.09 per cent octane (by calculation), which shows that considerable fractionation has taken place with consequent increase in relative proportions of the two more volatile components. When this gas is compressed to 100 lbs. per sq. in. gage and cooled to 20° C., the equation predicts a condensation of 56 per cent, while the condensation should yield 73 per cent of the total solvents, according to the calculation based on original average molecular weight.

One other example may be offered to show the application of the equation for three or more components. In dealing with benzol vapor it is usual to treat the benzol as if it were pure benzene. The usual solvent benzol, known as "90 per cent benzol," actually contains about 84 per cent benzene, 13 per cent toluene, and 3 per cent xylene. If we consider a gas mixture containing 15 per cent by volume of "90 per cent benzol" of this composition, and cool it to 20° C. at atmospheric pressure, the equation predicts a condensation of 50 per cent of the weight of the benzol, whereas for pure benzene the calculated value is only 38 per cent.

We realize that no *direct* experimental evidence is adduced to show the validity of the equations developed, but, on the other hand, they are based on nothing but very simple and well-established laws, and furthermore, they do lead to results which are in general accord with experience in the field of solvent recovery.

Early Chemical Industry in America—A Few Comparisons of Past and Present Conditions[1]

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THE SUBJECT "Early Chemical Industry in America" may perhaps appear a misnomer, for what is known to-day as chemical industry, with its organization of chemists for research and control, is of very recent origin. It has been said that there were no industries in the United States that could be termed strictly chemical until after the Civil War, and this is probably true if we limit our meaning to those industries that are controlled by chemical supervision. Chemical control requires a quantitative inventory of this or that valuable ingredient as it enters and leaves a factory, and quantitative analysis was not generally taught in American colleges until after the Civil War. It was only in private laboratories, such as that of Dr. J. C. Booth in Philadelphia, that such instruction could best be acquired. Probably no one did more than Dr. Booth toward making American manufacturers realize the importance of chemical control, yet this leader, as late as 1860, was unable to induce the iron masters of Eastern Pennsylvania to contribute jointly the small annual sum of $1200 for controlling the work of their furnaces by a chemical analysis of the ores.[2] Such was the general attitude of industry toward chemistry in the United States only sixty years ago.

But while chemically controlled industry in the United States is relatively modern, a large number of industries were established before 1800 which present nomenclature would term chemical. According to a report made by Coxe[3] in 1792, the following chemical industries were existing at that time in the United States: candles and soap; chemicals (such as Glauber salts, saltpeter, etc.); distillery products; drugs; fermentation products; glass, bricks and pottery; gunpowder; indigo; leather; lime and plaster; metals; naval stores (turpentine, tar, rosin, etc.); oils, fats, and waxes; paint and varnish; paper; potash; salt; sugar, molasses, etc.; and various miscellaneous products, such as glue and lampblack. In the present paper a brief account will be given of the rise of a few of these early chemical industries.

The Indians

The early pioneers of industry in this country were in many ways indebted to the Indians, who gave them their first knowledge of rubber, maple sugar, chocolate, vanilla, cochineal, and other commodities. The more advanced Aztec and Inca tribes had acquired a considerable knowledge of dyeing and other chemical operations. The modern chocolate manufacturer, for example, simply repeats on a large scale the various steps of curing, roasting, crushing, and rolling as they were first learned from the Indians. Another illustration of the chemical technology of the American aborigines is the manufacture of tapioca starch from Cassava. The crushed roots of this plant contain from 0.02 to 0.03 per cent of hydrocyanic acid, owing to the hydrolysis of a poisonous glucoside. The Indians, without knowing the chem-

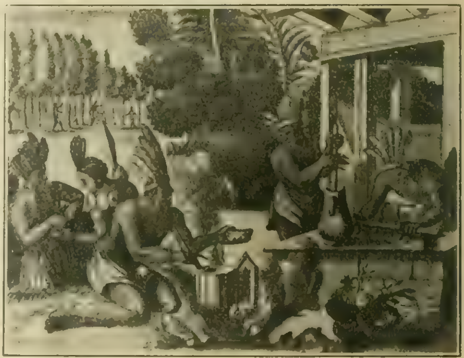

Fig. 1 Indians Roasting, Pounding, and Rolling Cacao Beans in Manufacture of Chocolate. (From Ogilby's "America," London, 1671)

istry of all this, first reduced the Cassava roots to a pulp on a rude grinding machine, then washed the starchy material in a pan, after which the poisonous water was removed by filtering through a sack and squeezing. The residue of starch was then dried. Other examples could be cited to show that many operations of modern industrial chemistry, such as roasting, grinding, pounding, washing, filtering, and drying, were performed by the Indians, although of course on a very primitive scale.

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[1] Condensed from two papers read before the Section of History of Chemistry at the 63rd Meeting of the American Chemical Society, Birmingham, Ala., April 3 to 7, 1922, and before the joint meeting of the New York local chemical societies [illegible] of the American Section of the Société de Chimie Industrielle, New York, N. Y., May 12, 1922.

[2] "Notes and Comments," by James M. Swank, Philadelphia, 1897, p. 151.

[3] "View of the United States," 1794.

THE SPANIARDS

The first Europeans to conduct experiments in chemical industry within the present borders of the United States were the Spaniards. Their inquiries were limited almost entirely to the precious metals. De Soto is said to have had metallurgists in the expedition which he led through the southern states in 1539 and 1540, and ancient diggings in Alabama are thought by some to have been made by De Soto's party. No records, however, of the metallurgical operations of this expedition have been discovered. The earliest definite account which the author has thus far been able to find of a chemical operation performed within the present boundaries of the United States is an unpublished report,[4] in a transcript of documents from the Spanish archives.

In the latter part of the year 1598, during the expedition of General de Oñate into New Mexico, a party of Spaniards noticed some bright-colored pigments of blue, green, yellow, and red, which the Indians were using. Suspecting that these pigments might be ores of precious metals, several Spaniards had the Indians conduct them to the source of the minerals, which was a three days' journey distant. Here with their knives they dug out lumps of ore which were carried back to the pueblo where the main body of the expedition was staying. The ores were assayed at this pueblo by an accountant, Alonzo Sanchez, and a purveyor, Diego de Cubia. These two officers made separate assays and reports. The deposition of Alonzo Sanchez is the more complete and, in substance, is as follows:

> From a stone received by Sanchez from the soldier Miguel Montero, and which weighed half a pound, more or less, he obtained in an assay, made by treating the stone with mercury for 8 days and then expelling the mercury, a lump of silver equivalent to about 12 ounces, more or less, to the quintal (or hundred weight) of ore. Sanchez stated, however, that because the assay was made during a spell of very cold weather and for only 8 days, he felt absolutely sure that the ore contained much more silver than he was able to extract. From his extensive past experience in the assaying of other ores by means of mercury, he believed the present mineral to be very rich in silver.

While this analysis by Alonzo Sanchez may lack something as regards exactness, his record should be allowed to stand until an earlier and better one is discovered. Ruins of old furnaces in Arizona and New Mexico indicate that mining and smelting operations were carried on there by the Spaniards at a very early date.

With regard to the extraction of silver from ores by mercury as mentioned in the old document of the Spanish Archives, it should be recalled that in 1557, forty years before Onate's expedition, the cold amalgamation, or *patio*, process of silver extraction was invented at Pachuca, Mexico, by Bartholomew de Medina.[5] This process, which for several centuries yielded the greater part of the world's production of silver, ranks as one of the most remarkable discoveries in metallurgy. It was particularly adapted to districts where fuel was lacking. In this process the silver ore, in the form of sulfide or other combination, was finely pulverized in a stone drag mill, or *arrastra*, which was the earliest form of pulverizer to be used in the western states. The wet powdered ore was then thoroughly mixed in a *patio*, or paved court, with common salt and the so-called *magistral*, which consisted of roasted copper pyrites. After the wet mass, or *torta*, had stood for some days, mercury was added and the whole well mingled together by tramping mules. At the end of a month or more, the earthy matter was washed away from the amalgam and the silver recovered from the latter by pressing through skins and retorting. The *patio* process, as Humboldt once remarked, is one of those chemical operations which were discovered and worked for centuries before the theory of the procedure was understood. Humboldt and Gay-Lussac spent much time in studying the chemistry of the process, and even now opinions differ as to the series of reactions in the *torta* by which the silver sulfide is changed to the chloride and the chloride to metallic silver. The *patio* amalgamation process and the Bustamente mercury furnace are among the first of the long series of industrial chemical processes which originated in the New World. The scientific work of the old Mexican metallurgists is not to be despised. It was a Mexican, del Rio, who first called the attention of the world to the element vanadium.

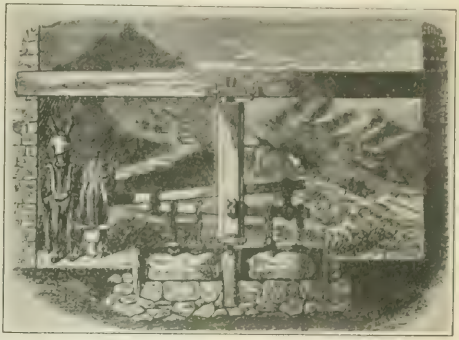

FIG 2—MEXICAN ARRASTRA, OR STONE DRAG MILL, FOR PULVERIZING SILVER ORES (FROM PEPPER'S "PLAYBOOK OF METALS," LONDON, 1862)

Over a century after the early work of the Spaniards in the Southwest came the smelting operations of the French in the old territory of Louisiana. In 1712, Louis XIV, king of France, looking with covetous eyes upon the precious metals which the Spaniards were acquiring in the New World, granted letters patent for developing the gold and silver mines of Louisiana. This was the origin of the famous Mississippi Bubble which afterwards burst and brought ruin to so many. The so-called "Company of the West" was formed and in 1719 a French metallurgist, Philip Renault, sailed from France with two hundred workmen. At San Domingo, Renault purchased five hundred slaves to work his mines, and then sailing up the Mississippi River arrived in 1720 at Kaskaskia, a French settlement in Illinois. From here he conducted prospecting expeditions, on one of which the famous lead mines[6] of Missouri were discovered. Renault, disappointed in his quest for gold, turned all his attention to lead smelting, and extracted considerable quantities of this metal which, after transporting by pack horses to the Mississippi and sending by boat to New Orleans, were shipped to France. But the inhability to find gold and silver created such disappointment in Europe that the charter of the "Company of the West" was cancelled and Renault was left without means to continue his work. He returned to France with his workmen, his slaves were sold, and the lead mines abandoned. In 1762, when Louisiana was ceded to Spain, lead smelting at the Missouri mines was revived, but the methods of extraction were imperfect and not more than fifty per cent of the lead in the ore was obtained. It was not until after the Louisiana Purchase in 1803, and the entrance of Americans into Missouri, that the methods of extraction were improved.

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[4] The report is entitled "Relacion de los ensayes que se hicieron de ciertas minas" and can be found in the Library of Congress at the end of Vol. III of the Lowery transcripts of documents relating to New Mexico in the Spanish Archivo General de Indias at Seville. The report is referred to on page 208 of H. E. Bolton's "Spanish Explorations in the Southwest."

[5] For a full account of this process see Humboldt's "Political Essay on the Kingdom of New Spain," Black's Translation (London, 1811), Vol. 3, pp. 253–280. See also Pepper's "Playbook of Metals" (London, 1862), pp. 213–216, which gives a good illustration of the *arrastra* and a scheme of the complicated chemical reactions which take place in the *torta*. For a more modern view of these reactions see the article by Vondracek, *Rev. metal.*, **5** (1908), 678, and the recent works on the metallurgy of silver.

[6] For a history of early lead smelting in Missouri see Schoolcraft's "View of the Lead Mines of Missouri," New York, 1819, which gives a full description of processes and illustrations of furnaces.

The furnace used by the French and Spaniards was of the simple log hearth type built upon a slope. The fuel consisted of oak logs, which, after filling in with the sulfide ore, were lighted. The sloping gutter of the hearth carried the melted lead into a pit below the front, from which it was ladled into iron molds and cast into pigs. After the entry of Americans into the field, the slag from the log furnaces was resmelted in a so-called "ash furnace," which consisted of a hearth with a long sloping flue. The lead slag was washed from wood ashes, crushed, mixed with a siliceous flux, and then fed into the top of the flue. The heated charge as it reached the bottom of the flue was melted; the fluid slag above the metal was drawn off on one side of the hearth and the lead tapped into molds on the other. The ash furnace was a great improvement over previous methods, but it was also primitive and wasteful and long ago went its way with other relics of the past.

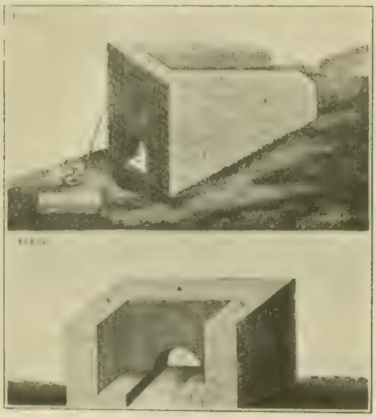

Fig. 3—Log Hearth Furnace for Smelting Lead Ore. (From Schoolcraft's "View of the Lead Mines of Missouri," New York, 1819)

The English

Industrial chemistry before 1800 reached a higher development in Massachusetts than in any other North American state or colony. In 1792 Massachusetts led in the exportation of nineteen chemical commodities, New York followed with seven, and Pennsylvania with five. Before 1800, Massachusetts led in the number of chemical patents, Pennsylvania was second, and Connecticut was third. The lead in industrial chemistry which Massachusetts held for over 150 years originated with one of its early colonists, John Winthrop, Jr., who landed in Boston in 1631 at the age of twenty-five. He is the man who deserves to be known as America's first industrial chemist. His interest in chemistry is shown by the fact that only a few months after his arrival he began to receive from England chemicals and apparatus for starting a laboratory. It is remarkable what Winthrop attempted to do in the establishment of chemical industries in the New England colonies. He was interested in the production of salt, iron, glass, potash, tar, black lead, saltpeter, copper, alum, and other chemicals. He read reports upon some of these industries before the Royal Society, of which he was a member, and these are the first contributions to be made by an American chemist before a scientific association. In view of the present efforts to establish a home dyestuff industry, it may be of interest to know that Winthrop and his uncle, Emanuel Downing, made what were probably the first experiments upon the manufacture of indigo within the present border of the United States.

In the library of the Massachusetts Historical Society of Boston, among the unpublished papers of John Winthrop, is a document[7] which should be of great historic interest to chemists. It is Winthrop's outline of a plan, the first of the kind in America, to form a chemical stock company, and reads in part as follows:

> If any desirous to promote a publique good shall see cause to accomodate that businesse with a stock of 3000 £ or 4000 £ I shall indeavour (God permitting) to raise such commoditee as may be convenient for returnes, and in particular that staple of saltpeter of which some (blank) of tunes are yearly carried into England, Holland, Portugall and other parts; and that no adventure of detriment may be to any, doe hereby ingage that the said stock shalbe within (blank) yeares duly repaied to them, with some convenient consideration (if God please to add a blessing to the designe so farre as it be profitably effected); and when it shall appeare demonstratively incouraging, they may, if they please to joyne in the business and to a further proceeding, advance to a stock of 10,000 or 20,000 £ or more.

Winthrop had a clear idea of the importance of saltpeter manufacture as a basic protective industry. Through his influence, in 1642, the General Court of Massachusetts passed an order for promoting the public safety to the effect that in order to raise and produce such materials "as will perfect the making of gunpowder, the instrumental means that all nations lay hould on for their preservation....every plantation within the Colony shall erect a house in length about 20 or 30 foote, and 20 foote wide within one half year next coming....to make saltpeter from urine of men, beastes, goates, hennes, hogs and horses dung."

This ordinance may be said to mark the birth of our modern nitrate and munition industries. The correctness of this early colonial policy was afterwards exemplified in the days of the American Revolution, when a Congressional Tract upon the manufacture of saltpeter was issued by John Hancock in 1776. As a result of this tract and the methods therein described, the manufacture of saltpeter and gunpowder made such rapid advancement that when the Revolution was over these commodities appear as articles of export.

In the war of 1812, the recently discovered nitrate deposits of Mammoth Cave and other caverns were used as a source of saltpeter. The process of manufacture,[8] as carried out at Mammoth Cave, was as follows:

> The "peter earth," containing about four pounds of calcium nitrate to the bushel, was gathered in sacks from the remoter parts of the cave and brought to the leaching vats, transportation being accomplished so far as possible in wagons drawn by oxen. The leaching vats were 12 to 15 feet long, 8 to 10 feet wide and 4 to 5 feet in depth; the bottoms of vats consisted of logs cut from small trees, split into halves and hollowed out, and joined together so that the upper logs with convex surfaces up fitted into the grooves of the lower logs with convex surfaces down. The water for leaching the earth was brought in wooden pipes, made by boring through the long stems of trees, from a spring outside the cave. The leachings were caught in the grooves of the lower logs which being slightly inclined conveyed the dilute solution of calcium nitrate forward into a channel to a reservoir whence it was pumped through another wooden

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[7] Winthrop papers, Vol. 5, p. 9.

[8] An account of the nitrate caves of Kentucky and other states and details of the method of manufacturing saltpeter are given by James Cutbush in his "System of Pyrotechny" (Philadelphia, 1825), p. 54.

pipe to the outside of the cave. Here the leachings were evaporated in kettles and the strong solution filtered through hoppers containing wood ashes. The calcium nitrate was in this way converted into potassium nitrate, which was crystallized from the filtrate, after again concentrating and cooling in wooden troughs. The crystals of potassium nitrate after drying were packed and transported by horses and mules to the seaboard.

Fig. 4—John Winthrop, Jr., in Early Life. (From an Old Portrait Reproduced in T. F. Waters' "Sketch of the Life of John Winthrop the Younger")

Economic Factors

It is impossible within the limits of the present paper to extend these descriptions to the manufacture of potash, salt, iron, soap, paper, glass and other products, but a brief reference should be made to a few economic factors which influenced the growth and development of early American chemical industries.

There are still vivid recollections of the effects of the recent World War upon chemical industries in the United States,—of the extraordinary stimulus which was at first produced, of the brief but wonderful prosperity which ensued, of the terrible depression that followed, and of the strenuous efforts made to save the new industries which the war called into existence. Yet these recent events are relatively of minor significance when compared with what happened in the United States between 1806 and 1826. In order to understand the events of this critical period it is necessary to go back to colonial times.

The early Trading Companies, such as the "Company of the West" already mentioned, the "West India Company," and others, financed and started their colonies in the New World as simple business propositions. The "London Company," for example, sent over English, Polish, and German workmen to Jamestown in 1608 to make pitch, tar, and potash, and to exploit the country for metals, drugs, dyes, and other products. The mistake was made, however, of beginning manufactures too soon. The shareholders of the trading companies hoped for an immediate return on their investments, and, when the first settlers forsook industry for agriculture, were naturally disappointed. They had, however, lost sight of the fact that the basic needs of food, shelter, and clothing come before glass, potash, and iron. When the laborers who had been sent over tore up their indentures and forsook the furnace for the field, they were simply obeying a natural law, expressed upon the seal of one of our National Departments, that "agriculture is the foundation of manufacture and commerce." It was only after building his house and planting his fields that the early settler could turn his attention to simple industrial pursuits.

The manufacture by the colonist of simple products for his personal and domestic needs marked the first stage in the development of American industrial chemistry. The pioneer tanned his own leather, forged his own iron, made his own potash and soap, curdled his own cheese, dyed his own wool, and boiled his own sugar and salt. The processes were crude but they marked the inception of that idea of industrial independence which afterwards became of such momentous importance, and which, similar to that other idea of political freedom, was the natural birthright of every pioneer.

As the country became more thickly settled, there was the natural division of labor, which always comes with social advancement, and this resulted in the second, or coöperative stage of American industrial chemistry. The farmer took his hides to the tanner to be made into leather, his homespun to the fuller for dyeing, and his tallow to the soapboiler for making into soap. He exchanged his farm products with the iron maker for unfinished rods which he wrought at home into nails or staples according to his needs. The intimate coöperation of agriculture and industry had an important bearing upon the shaping of policies in this country. There was a solidarity and unanimity of feeling between the farmer and manufacturer which unfortunately ceased when this coöperative period came to an end.

Effect of Colonial Troubles with England upon Chemical Industry

The great fundamental difficulty between Great Britain and the American colonies was whether the latter should send their raw materials to England to be manufactured into the finished products which they needed, or whether the colonies should save themselves from this exploitation by utilizing their own natural resources. The passage, before the Revolution, of the Stamp Act caused the feeling of industrial independence, which had been constantly growing, to assert itself; the colonists voted in retaliation to import no more refined sugar, leather, starch, linseed oil, glue, glass, metalware, paper, dyed goods, or any other product which they could manufacture for themselves. The principle of industrial independence was considered to be worth defending, and when its recognition was won at Yorktown, steps were taken to secure the victory by necessary Congressional legislation. Through the wisdom of Hamilton our first protective tariff was passed; additional stimulus was given to industry by the establishment of patents; the different states awarded bounties and granted exemptions to start glass and other chemical manufactures; prizes were awarded by the numerous societies that had been formed to stimulate domestic production. Industry grew, commerce increased, and American ships began to appear on every ocean.

If the right of Americans to do their own manufacturing was one of the leading motives of the Revolution, the right to carry their manufactured products to other nations without hindrance was the chief motive which inspired the war of 1812. During the Napoleonic wars between 1806 and 1812, the position of the United States greatly resembled that in the recent European war between 1914 and 1917. Our manufacturers were first stimulated to supply the needs of foreign contestants. The start, thus acquired, received an immediate impetus in 1806 by the passage of an embargo upon the importation of British goods, and was still further intensified between 1812 and 1814 when the United States became involved in a conflict with Great Britain owing to interferences with American commerce.

After the downfall of Napoleon and the declaration of peace between the United States and Great Britain, the latter nation, with its thousands of discharged soldiers returning to the fields of industry, set out to recover its lost markets. Great Britain, by the early adoption of the steam engine and other labor-saving machinery, had at least a twenty-year start over other nations in the contest for industrial supremacy. She had not only the skilled labor and the shipping, but she could turn out products in such quantities and at such low prices that competition was impossible. Great Britain was even ready to export products at a loss. Lord Brougham, in a speech before Parliament in 1816, declared, "It is well worth while to incur a loss upon the first exportation, in order by the glut to stifle in the cradle those rising manufactures in the United States, which the war has forced into existence contrary to the natural course of things." British products were shipped to New York for immediate sale at auction, and, before anti-dumping laws could be passed, an almost irretrievable damage had been inflicted upon American manufactures.

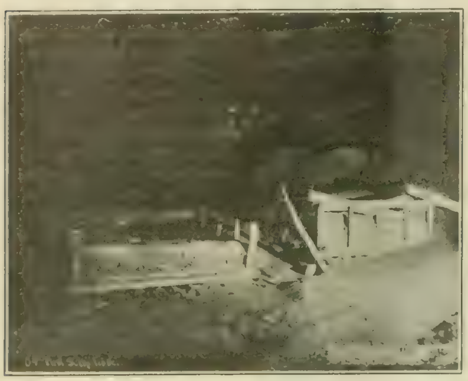

FIG. 5—NITRATE VATS IN MAMMOTH CAVE, KY., USED IN 1812. (PHOTOGRAPH SUPPLIED BY M. B. WADE, RUSSELLVILLE, KY.)

The influence of these events upon our chemical industries can be illustrated in no better way than by following the course of chemical patents. The number of patents taken out in a given industry is an accurate index of the prosperity of that industry and the variation in the annual number of chemical patents from 1790 to 1840, shown in the diagram on p. 1071,[9] gives a concise and reliable picture of the progress of chemical industry during this important fifty-year period.

In the diagram the continuous line represents the population of the United States as expressed in millions and the broken line the number of chemical patents. The two lines are fairly coincident until about 1802, when there is a sudden rise in the patent curve. This rise is due to the temporary repeal in 1802 of the duties upon stills and distillery products, and the increase at this point is for improvements in distilling and rectifying. In 1806, owing to interferences with American commerce, an embargo was placed upon the importation of British goods and a stimulus was imparted to American chemical manufactures which reached its climax during the war of 1812 to 1814. The years 1815 to 1824 marked the period of dumping cheap foreign goods upon unprotected American markets; and, as the diagram shows, the incentive to take out chemical patents was lacking. In 1824 the first effective tariff law was passed, and from this time dates the well-known "American System" of Henry Clay, the savior of American industries. The benefits of the "American System" lasted until 1836, when the growing opposition of the agricultural states of the South to tariff laws for the protection of industry resulted in the passage of compromise acts. These had a bad effect upon manufacturing and with the bank troubles and financial panic of 1837 plunged American chemical industries into a second long period of depression.

If there were time, it would be interesting to trace the development of the chemical industries which sprang into existence in the United States as results of the embargo of 1806 and of the war of 1812. Their development is reflected in the character of the chemical patents. Previous to 1806, these patents related chiefly to the old colonial industries of distilling, salt manufacture, potash making, and the utilization of sperm oil and other fats for soap and candles. But after 1806, when the importation of foreign goods was restricted, the inventive genius of American chemists began to be diverted into more modern channels. Between 1806 and 1814 there are noted for the first time inventions that relate to subliming sulfur, dyeing silks and calicoes, bleaching, refining camphor, waterproofing leather, making artificial mineral water, and manufacturing sulfuric acid, copper acetate, magnesia, and white and red lead. The year 1806 marks the awakening of industrial chemistry in the United States. The first American students, Benjamin Silliman and others, were returning from their chemical studies in Europe and contributed their share to the new movement. American publishers began also about this period to print practical treatises upon chemistry—works of native writers such as Dr. Thomas Ewell, and reprints of European authors such as Frederick Accum—and for the first time the attention of the public was called to the national importance of chemical industries.

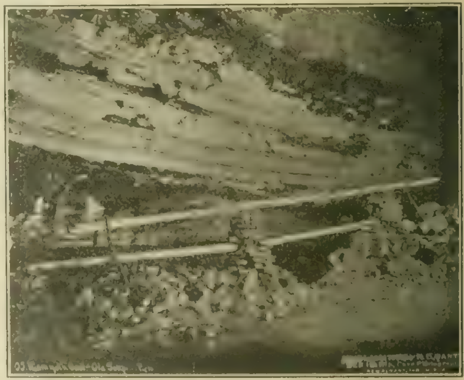

FIG. 6—WOODEN WATER PIPES FOR TRANSPORTING WATER AND NITRATE LEACHINGS IN MAMMOTH CAVE, KY. (PHOTOGRAPH SUPPLIED BY M. B. WADE, RUSSELLVILLE, KY.)

EARLY STRUGGLES FOR PROTECTION

It is a singular fact that the battle for domestic chemical industries, after the war of 1812, was waged largely, as it is being waged since the recent European war, upon the question of dyestuffs, and it is also singular that it was fought one hundred years ago, as it is being fought now, largely upon the issue of patriotism. When foreign dyed fabrics threatened the extinction of the domestic industry after the war of 1812, there sprang into existence a host of patriotic societies whose battle cry was that American dyed clothing, no matter how poorly colored, should be worn as a badge of honor, and it was so worn, although, as Daniel Webster and many others testified, the blues on a rainy day washed out of their new outer garments until their shirts and skins looked as though they had been dipped in an indigo pot. The American color chemist one hundred years ago was new at his business, but he persevered and won out, just as his modern colleague is persevering and winning out to-day.

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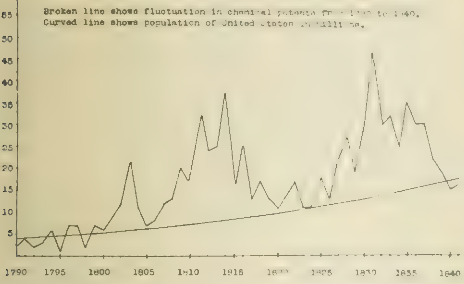
[9] In con[illegible] made of Class 4 of the "List of patents issued [illegible] 1790 to 1847," compiled by Edmund Burke, Commissioner of Patents, Washington, 1847. Class 4 (pp. 99–119) comprises all patents relating to "Chemical Processes, Manufactures and Compounds."

A year or so ago an incident[10] of almost international importance was produced by the arrival of several German color chemists to initiate certain American manufacturers into the secrets of their trade. Similar happenings took place after the war of 1812, and measures were taken by Great Britain at that time, as by Germany to-day, to prevent the exodus of her chemists and the transmission of trade secrets to the United States.



Progress of American Chemical Industries as Shown by Chemical Patents

1802–1804: Temporary repeal of duty on stills. Increase in distilling patents
1806–1809: Stimulus of chemical industries due to embargo
1812–1814: Increase in chemical industries during war of 1812
1815–1824: Dumping foreign goods. Depression in chemical industries
1825–1836: Increase of chemical industries under "American System"
1837–1840: Depression in chemical industries after panic of 1837

The opportunities of better wages and living conditions nullified, however, the power of such enactments. The best European technologists began to flock to the United States after the war of 1812, and the knowledge and skill which were thus acquired played no small part in the upbuilding of American chemical industry.

It is impossible to give a complete sketch of the battles which were fought for the protection of our early chemical industries. It is unfortunate that the lessons of these battles seem never to have been learned. The conflict has had to be fought over and over again and the battle must always be repeated until the regulation of the tariff is taken from politicians and placed in the hands of a permanent commission.

The lessons of the first great battle to preserve our chemical industries were summarized for all future time in a report of chemists who met at an industrial convention in New York in 1831. It is significant that this first general meeting of American chemists was purely industrial in character. Although their report[11] refers solely to the war of 1812 and its after-effects, their words are equally applicable to the war of 1914 to 1918 and the subsequent period. The following paragraphs are quoted:

> Intimately connected with science and the healing art, and essential to other manufactures, chemistry received very little or no attention from the enterprise and skill of our country, until the late war. That event suddenly cut off the usual supplies from foreign countries. The consequent advance in price was excessive, and the inconvenience sustained by that class of manufacturers who consumed chemicals, incalculable. This state of things gave the first impulse to chemistry in our country.
>
> The return of peace, however, brought foreign competition which soon threatened to extinguish the infant and yet inexperienced establishments which had crept into existence during the war. The large importations which, at that period, inundated the country, caused a reduction in prices, alike ruinous to the importer and his competitor, the American manufacturer.
>
> This depression, however, would have been but temporary, had there been no interference on the part of the government. The foreigner would have prevailed in the contest—and the market becoming his, the prices would have been in accordance with his own remorseless interests.
>
> Happily for the nation, and more particularly for that numerous laboring class who are dependent on chemical manipulations—and the agriculturists, who find in this class a customer instead of a rival—happily also for the other classes of manufacturers who owe their existence to chemistry, the tariff act of 1824 placed the seal upon the policy of the nation. By this act, and not until after its passage, was the manufacture of chemicals established in the United States.
>
> Until it became the policy of the nation to encourage a domestic supply of chemicals, prices were constantly fluctuating—were generaly high and oftentimes seized upon for purposes of speculation, to the great injury of consumers. Domestic competition has caused prices to settle at a minimum rate. The manufacturer is now so near the consumer that his wants are anticipated and scarcity is unknown—because the raw material, being unlimited in quantity, and individual enterprise commensurate with it, the demand is seldom allowed to overtake the supply.
>
> The large consumption caused by the growing wants of our country, if dependent on the laboratories of Europe, would have either enhanced prices or have justified the maintenance of former rates—for, until the business was undertaken in this country, the foreign manufacturers seem not to have discovered how cheaply they could work.

The above story of the depression which prevailed in the United States when the chemical industries established during the war of 1812 were nearly extinguished, and the revival of these industries under an adequate protective tariff should be remembered in the present times of trouble. The chemists who drafted the report of 1831 spoke from the vantage ground of bitter experience. Without knowing it they were writing prophecy, as well as history, and their plea for the independence of our American chemical industries should stand as a lesson for all time. The plea which they made was not a new one. In 1806, a quarter of a century before the chemical convention of 1831, Dr. Thomas Ewell of Virginia made a similar plea, and a passage[12] from his stirring appeal is quoted in conclusion:

> The time is now come when the citizens of America should act entirely for themselves; when they should forever cease to depend on the caprice of foreigners for the innumerable chemical compounds. This fair portion of the civilized world, to have its beauties enjoyed, and its excellencies duly appreciated, must in all its parts be adorned by native chemists.

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[10] See *New York Times*, January 6 and 16, February 21 and 22, 1921.

[11] This Journal, **9** (1917), 177.

[12] "Plain Discourses on the Laws or Properties of Matter, Containing the Elements or Principles of Modern Chemistry," by Thomas Ewell, M.D., of Virginia (New York, 1806), p. 30.

Civil Service Examination

Assistant in Home Economics (food investigation), to be held on November 8, 1922, to fill a vacancy in the States Relations Service at Washington, D. C., at $1800 to $2220 a year. The duties of the appointee will be to conduct investigations in regard to any phase of household preparation and preservation of food materials which may be required to be studied. Competitors will be rated on (1) practical questions based upon the subject matter of bacteriology, chemistry, and physics as applied to the problem of home economics, and upon the subject matter and methods of experimental cookery, (2) thesis, and (3) education, training, and experience.

German-United States Competition in World Markets[1]

By G. B. Roorbach[2]

HARVARD UNIVERSITY, SCHOOL OF BUSINESS ADMINISTRATION, CAMBRIDGE, MASS.

FEAR has been expressed repeatedly since the armistice that United States manufacturers could not meet German competition in selling manufactured goods in world markets; not only that, but that the United States itself would be flooded with German wares to the detriment of American production. The fact that such a "flood" of imports into the United States has not materialized and that the export trade of the United States during the past three years has more than held its own in comparison with other nations, has apparently not removed the belief that German competition in manufactures is a black cloud overshadowing our commercial revival. That there is no competition with Germany to be met and respected, no one acquainted with the facts will deny; but that the force of this competition has been greatly overemphasized and that much of the fear is groundless, is also clear.

Much of the fear in regard to meeting German competition has been based on the following arguments:

(1) There had been an accumulation of goods in Germany during the war, ready for dumping in foreign markets.

(2) German industrial recovery, it was stated, was bound to be rapid, and German factories would turn out goods at a rapid rate and at less cost than most of her rivals.

(3) Germany's ability to undersell in foreign markets would be greatly facilitated by the depreciated exchange value of the mark, currency inflation within Germany, and the generally abnormal conditions of trade and exchange.

Let us examine the force of these reasons in the light of the experience of the past two years and the present situation existing in Germany.

(1) That Germany did not have large accumulations of exportable goods waiting to be dumped into foreign markets on the first favorable opportunity has been demonstrated by the events of the past three years. German export figures give no indication that there were large stocks waiting shipment. The nearest approach to this condition was possibly in the case of toys. It is probable, also, that the embargoes against German dyes and chemicals in Italy, the United Kingdom, and the United States prevented much larger exports of these articles, but, taking trade as a whole, Germany has been found to have a deficiency, not a surplus, of exportable goods. German agents booked many orders in foreign countries, but German factories have been unable to fill them. If we compare the export trade of Germany for 1921 with pre-war years, we find that where German exports in 1912 were valued at 8,956,000,000 gold marks, and in 1913 at 10,096,500,000 gold marks, for the last eight months of 1921 they were valued at 4,591,000,000 gold marks (statistics for the whole year not available). In volume the corresponding figures were:

1912	67,331,900 tons
1913	75,432,000 tons
1921 8 months	13,721,160 tons

During the first half of 1922 there was a tendency to an increase in exports, but the June and July exports in tons have again declined to the 1921 average. Monthly trade statistics are given in the following table:

FOREIGN TRADE OF GERMANY, MONTHLY AVERAGES[1]

YEAR AND MONTH	MERCHANDISE			
	Imports		Exports	
Monthly Average:	In Millions of Marks	In Thousands of Metric Tons	In Millions of Marks	In Thousands of Metric Tons
1913	890	6,073	841	6,141
1920	...	1,570	5,776	1,651
1921	9,910	2,194	8,295	1,715
1921:				
July	7,572	1,925	6,175	1,558
August	9,382	2,111	6,670	1,828
September	10,642	2,533	7,492	1,871
October	13,814	3,005	9,681	1,973
November	12,273	2,535	11,886	1,908
December	13,702	2,086	14,468	1,930
1922:				
January	12,641	2,309	14,394	2,027
February	12,001	1,475	14,482	1,747
March	22,919	2,645	21,285	2,153
April	28,266	2,889	22,948	2,760
May	32,417	3,810	27,080	2,093
June	34,364	4,030	30,232	1,880
July	45,738	4,798	35,707	1,636

[1] *Federal Reserve Bulletin*, September 1922, p. 1102.

The following table gives a comparison for certain commodities, mostly manufactured, for 1912 and the second half of 1921. Exports were probably greater the second half of the year than during the first half.

PRINCIPAL ARTICLES EXPORTED FROM GERMANY IN 1912 AND THE LAST SIX MONTHS OF 1921[1]

ARTICLES	1912	July–December 1921
	Metric quintals	
Aniline and other coal-tar dyes	596,960	117,196
Automobiles, passenger	92,250	86,013
Chinaware, including insulators	493,980	131,858
Coal, bituminous	311,450,570	35,026,511
Copper and alloys, and manufactures	882,340	192,816
Cotton fabrics	1,256,310	201,872
Clothing, millinery, and other sewn articles	98,700	48,108
Electrical apparatus:		
Dynamos, motors, and transformers	352,630	79,127
Electrical appliances for illumination, transmission of power, and electrolysis	158,980	79,319
Glass, hollow	1,568,870	333,116
Iron and steel, and manufacture	32,617,440	13,398,033
Rails for railways, sleepers, fishplates, and bedplates	8,262,860	1,824,816
Leather, and manufactures	99,860	42,760
Leather, upper, for boots, shoes, and slippers	96,890	18,686
Machinery of all kinds, except electrical	5,062,900	1,896,840
Paper and cardboard, and manufactures	4,391,010	1,867,622
Potash salts and abraum salts	13,004,570	2,602,200
Toys and Christmas-tree decorations	524,680	374,668
Woolen fabrics	718,410	147,882

[1] *Trade Information Bulletin* **40**, Bureau of Foreign and Domestic Commerce.

It is true that when trade with Germany was resumed there were times when quantities of German goods were suddenly dumped in certain markets, and temporary consternation resulted in the industries affected. But those sales were like bankruptcy auction sales, temporarily disturbing to the local market and causing embarrassment to local merchants. Unemployment in industrial countries to-day cannot, except possibly in rare instances, be traced to German competition. In a country like England, for example, unemployment, as far as it is affected by Germany, is due to the lack of commercial prosperity in Germany, rather than the reverse. English mills might be more fully employed if the German market for English goods could be brought back to its pre-war status, but Germany is a poor purchaser under the present abnormal economic and financial conditions that there exist.

(2) The ability of German factories to manufacture on a large scale for export, and at prices so low that they could not be met by foreign competitors, has been greatly overestimated. Much of Germany's post-war industrial activity was in answer to her domestic needs. As in other countries, the war left German industrial and transportation equipment greatly run down.

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[1] Received August [illegible], 1922

[2] Professor of Foreign Trade, Harvard University, School of Business Administration

Much of the country's production has been needed for replacement, repair, and equipment, and consequently a smaller proportion of industrial production has been available for export.

The restriction of exports has been aided also by the tax system, causing manufacturers to invest heavily in equipment in order to avoid excess profit and other taxes. New taxes and the proposed enforced loans are bound to fall with increasing severity on German industry, giving an increasing burden that must inevitably add to manufacturing costs.

Furthermore, the constantly depreciating currency in Germany has encouraged domestic buying on an unprecedented scale. With the internal value of the mark declining, the German people have transferred their accumulated marks at once into tangible objects. There has been an enormous speculative buying at home, giving temporary support to industrial development that must stop whenever the mark ceases to decline in value.

Pre-war relations between production and exports, says Commercial Attaché Herring of Berlin in his reports to the Department of Commerce, are not being maintained. German industry as a whole is producing perhaps 60 per cent of its pre-war output, but a much less percentage of that production is entering export trade as compared to pre-war years.

Industrial production in Germany is handicapped by increasing difficulties in obtaining raw materials and fuel. Her colonies are gone and her home territory has been deprived of rich raw-material-producing sections. The curtailment of coal-producing areas, the necessity of delivering coal as part of reparations payments, strikes, and general unrest are resulting in coal shortages that are seriously interfering with iron and steel production and industry in general. Pig iron shortage is repeatedly reported. Importation of coal from Great Britain, at high prices, has been increasing in recent months and now exceeds pre-war imports. The most important raw materials imported—and Germany is dependent on many such—are very high in price because of exchange and credit conditions, and in some cases not obtainable at any price.

Nearly all other costs of production are rapidly increasing. Freight rates have been again and again advanced, and in June were reported 60 to 70 times higher than pre-war. Wage increases are constant, wage agreements not being made for a period longer than one month. In spite of wage increases, prices have so much more rapidly increased in Germany, that the German workman is actually underpaid and his efficiency is much less than formerly. The productivity of German labor, according to Commercial Attaché Herring, is less by 20 to 25 per cent than before the war, on account of the lowering of the standard of living. This is without reference to the eight-hour day now prevailing. It is evident that whatever advantages Germany had for cheap production for export immediately after the war were temporary. With each succeeding month these advantages have become fewer and less effective.

(3) Much emphasis has been laid upon the advantages accruing to Germany in selling abroad because of the depreciated exchange value of the mark. As long as the external value of the mark was rapidly falling and the internal value only slowly declining, whatever products Germany had available for export, it is true, had a decided advantage over countries with stable currencies. But at best such a condition can be only temporary, although while it lasts opportunity for dumping is large. It is an indication of economic weakness, however, and points its own destruction.

To save herself from exchange losses Germany early attempted to equalize export prices and world prices by adding an export tax sufficient to make the actual exchange price somewhere near the world price level. Trade that depends on a continuous depreciation of the exchange value of currency is on an exceedingly insecure foundation.

Currency inflation, such as has taken place in Germany, in connection with a greatly depreciated foreign exchange at first gave German products large price advantages in foreign markets. Domestic prices, transportation costs, and wages have, however, rapidly adjusted themselves in Germany until at present the disparity between German wages and prices and world wages and prices is slight. Further currency depreciation can be less effective in the future in producing a wide spread between world prices and German domestic prices. When further depreciation stops, inflation can of course be of no benefit to trade. In fact, to stabilize the value of the mark, not to mention improvement in its value, will be likely to result in widespread industrial depression in Germany. In the long run, currency inflation and depreciating exchange weakens a country's ability to compete in world markets. It is, of course, itself a sign of economic and commercial deterioration.

An indication of the rise in prices in Germany is given in the *Frankfurter Zeitung* Wholesale Price Index. As shown in the table below, prices on July 1, 1922, were more than double prices on the preceding January; and January 1922 prices were over 42 times those of 1914.

WHOLESALE PRICE INDEX, GERMANY

Frankfurter Zeitung

July 1, 1914	100	Nov. 1, 1922	5427
Jan. 1, 1920	1997	April 1, 1922	6722
Jan. 1, 1921	2127	May 1, 1922	7379
Jan. 1, 1922	4238	June 1, 1922	7841
Feb. 1, 1922	4612	July 1, 1922	9141
		Aug. 1, 1922	15,050

As a result of the instability of prices and wages caused by fluctuating exchanges and currency depreciation, trade, both foreign and domestic, becomes largely a speculation. Orders taken cannot be filled at agreed-on prices and contracts are cancelled. As German prices have approached world prices, new orders have declined. German industry is less and less able effectively to compete in foreign markets with nations whose financial, economic, and political conditions are on a surer, sounder foundation. For a time there was apparent industrial revival in Germany, and Germany's export trade for several months rapidly increased, as was to be expected with the coming of peace. But her trade has not reached anywhere near pre-war proportions, and conditions for production are such in Germany that it is difficult to see how Germany can very soon be a menacing factor in world trade.

If American exporters were able to meet German competition in pre-war trade—as they were in most lines—there would seem to be small grounds for fear at the present time. Germany has emerged from the war and its aftermath a defeated nation, shorn of all her colonies and much of her productive territory at home, saddled with colossal reparation debts, deprived of her merchant marine, struggling with internal economic, social, and political problems of the gravest character. That the United States with its vast resources, its strengthened industries, its impregnable financial stability, its superb industrial organization both for producing and for selling, should look forward with greater apprehension as to her ability to compete with Germany in world markets than she did before the war is incomprehensible.

The writer of this article has not at hand detailed information as to the present competitive power of Germany in the manufacture and sale of chemicals as compared with her power in pre-war years. The chemical industry has long been one in which Germany has had recognized advantages. The manufacture of dyes and coal-tar chemicals, particularly, had been brought to a high state of development, and Germany had, as is commonly known, almost a monopoly of world trade in many chemical products. There had thus developed in Germany a highly trained, expert force, an industrial organization and equipment of great magnitude, and a foreign market that reached every part of the world. That in this industry German competition with the outside world should have continued to be very effective after peace was established, is not to be wondered at. Possibly German chemical plants can to-day obtain trained technical men in large numbers at far lower wages than American firms can do; but this condition existed before the war, and the comparative advantage of Germany is no greater now. Probably, all things considered, it is less. It is undoubtedly necessary, if an American chemical industry is to develop, to give it protection from German competition; but, if the facts in regard to German competition in general as outlined in this article are true, we can more readily meet that competition to-day both at home and abroad, than we could in pre-war years. This is not to say that Germany is not able, in certain industries, to give effective, perhaps destructive, competition; but, with internal conditions as they are, that competition is less effective now than before the war.

German Competition[1]

As Affected by the Depreciation of the Mark

By E. A. Goldenweiser[2]

Federal Reserve Board, Washington, D. C.

GERMAN exchange during the month of September fell to 5 cents a hundred marks, compared with its pre-war value of 23.8 cents a mark. This extreme depreciation caused the Germans to turn to foreign currencies—mainly to the dollar—as a standard of value, particularly in drawing up long-term contracts, such as insurance policies, long-term loans, and the like. Even a court of justice recently rendered a decision declaring that, in view of the cataclysmic dislocation of German economic life, certain contracts drawn in pre-war marks cannot be satisfied by payment in paper marks, 1922 model. This decision gives official recognition to the fact that the mark is no longer a respectable member of the community of national currencies. The mark is thus declared an outlaw and fair game for sharp-shooting speculators.

Ever since the rapid decline of the mark set in soon after the armistice, there has been a widespread alarm among Germany's competitors at the danger of Germany underselling them in the world markets. This apprehension arose from the fact that the mark was much cheaper in the international market than in the domestic market, which means in simple terms that a dollar would buy more goods in Germany than in the United States, because the dollar could be exchanged for a sum in marks sufficient to buy a larger amount of goods in Germany than the dollar would buy at home. In other words, prices in Germany have not advanced as fast as the mark's exchange value has declined.

The depreciation of German exchange has kept many persons interested in international trade awake at night, and has resulted in widespread agitation for embargoes, high protective tariffs, American valuation, and similar efforts to deprive Germany and other countries with depreciated currencies of their alleged competitive advantage. This fear of commercial invasion has by this time largely subsided as a result of straight thinking and the nonappearance of the invader. With the minds of the people thus cleared of the economic fallacies involved in the panic fear of German commercial invasion, it may be worth while to point out some phases of the situation which make it advisable to combine with a full realization of the groundlessness of the panic a cautious attitude toward such competition as Germany may be able to offer.

While there is little danger of Germany conquering world markets under existing conditions, there may be the possibility of considerable competitive advantage for German manufactured products, at least temporarily, in certain lines of industry. The degree of this advantage may be estimated along the following lines:

(1) It is clear that industries depending on foreign raw materials will not benefit greatly by the depreciation of the mark, for they will lose in the purchase of the raw material whatever advantage they may have in the sale of the finished product. This eliminates a large part of Germany's export industry, which has always depended to a great extent on imported raw materials.

(2) The larger the labor cost in proportion to the total value of a product the greater will be Germany's temporary advantage arising from the depreciation of the mark. The reason for this may be briefly stated as follows: The wholesale price index in Germany on September 1 was about 29,000 on the basis of pre-war prices as 100, compared with an index of the value of the dollar expressed in marks of about 30,000 on the basis of the par rate of 4.2 marks to the dollar as 100, showing that so far as the wholesale market is concerned the price level in Germany has very nearly adjusted itself to the depreciation of the mark in the exchange market. A dollar would not buy much more in Germany at wholesale than at home; but this is not true to the same extent of the purchasing power of the mark in buying the necessaries of life for a family. The cost of living index in Germany in July, the latest available date, was about 5000, while the corresponding index of the cost of living in America converted to marks was about 8000, indicating that it cost more than one and a half times as much to support an American family as a German family, even though the index numbers presumably allow for the difference in standards of living. This means that the ultimate cost of labor entering into a manufactured product in Germany is much less than in America, and even allowing for the loss of efficiency through lower standards of living, it still remains unquestionably true that in certain industries, whose raw materials are of domestic origin and whose products derive most of their value from the labor expended upon them, Germany will have a competitive advantage over America as long as the mark has not been stabilized and the domestic price level has not adjusted itself to the depreciation of the mark.

(3) A factor in the situation is also the extent to which German manufacturers have an advantage in established trade connections, reputation, and previous control of markets. In such enterprises as the chemical industry, more particularly the production of dyes and the manufacture of toys, the Germans have the advantage of a world-wide reputation, together with established trade machinery which will help them make the most of whatever temporary advantage the exchange situation may afford.

(4) The German government's policy of subsidizing the public by keeping down rents and the price of food cannot benefit the country in the long run. This policy, however, may effect

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[1] Received [illegible]

[2] Associate Statistician, Federal Reserve Board, Washington, D. C.

a temporary reduction of labor costs and for the time being afford a certain advantage to such industries as are in a position to manufacture and export their products.

The fact that, generally speaking, Germany is not benefited by the present exchange situation is clearly indicated by the very continuance of this situation—paradoxical as this may seem. If Germany had a real competitive advantage as a result of her fallen exchange, she would have exported an enormous amount of merchandise, thereby creating a large demand for mark exchange and raising the rate on the mark in order to largely wipe out the previously existing advantage. Water tends to find its own level. But Germany was not able to export on a large scale, owing to lack of materials, lack of capital, and lack of confidence in domestic conditions; owing also to the efforts of many Germans to remove their liquid capital from the home country, to the prohibition of nationally unprofitable exports, to export taxes, to foreign embargoes, and to other factors all of which prevented the currency and price levels in Germany and abroad to become adjusted and equalized. It is true, therefore, that the continuance of Germany's *apparent* advantage in international trade is evidence that she has no *real* advantage.

Nevertheless, this does not mean that persons engaged in any industry that competes with Germany should be lulled into indifference and carelessness by the knowledge of Germany's predicament. Just as some Germans have made huge fortunes out of Germany's collapse, some German exporters may flourish on the ruins of Germany's economic structure. When in a railroad accident the number of casualties is small, this affords but little consolation to those who are crippled by the accident, or to the families of those who have lost their lives. Similarly, in the case of the catastrophe that befell Germany. The fact that relatively few foreign industries will be in danger from the crash should not prevent each person engaged in international trade from carefully scanning all the facts affecting his particular industry with a view to determining whether the combination of circumstances is not such as to endanger his markets, at least temporarily. In the long run there is no danger, but few businesses can be conducted with a view to the long run since business casualties are generally the result of short-run developments. An American exporter, after losing his all as the result of a temporary condition, while he had his eyes glued to long range possibilities, will find little comfort in the ultimate triumph of his American competitors who had watched to-day, to-morrow, and next week, as well as next month, next quarter, and next year.

Manuscript Bibliographies in Chemistry and Chemical Technology

Compiled by Clarence J. West and Callie Hull

RESEARCH INFORMATION SERVICE, NATIONAL RESEARCH COUNCIL, WASHINGTON D. C.

There exist many unpublished, or manuscript, bibliographies for scientific subjects which, if known and made available to investigators, would be effectively utilized. In view of this fact the Research Information Service, in coöperation with the Divisions of Science and Technology of the National Research Council, has undertaken to compile lists of manuscript bibliographies in the mathematical, physical, and biological sciences. A list for geology and geography has already been published as No. 27 in the Council's Reprint and Circular Series.[1]

The list presented for chemistry and chemical technology, although incomplete, should prove useful. It is hoped that it may also encourage those who possess unpublished bibliographies, as well as those who are in need of bibliographic lists, to coöperate with the Research Information Service by reporting their bibliographies and by inquiring as to the existence and availability of lists before undertaking independent compilation.

The fact that the information concerning each bibliography included in this list—period covered, method of entry and approximate completeness—is taken directly from the reports supplied to the Research Information Service, accounts for the incompleteness of the data in certain cases and for the evaluation of materials.

The Research Information Service is prepared to serve as a clearing house in connection with scientific and technological bibliographies. Those who prefer, however, may correspond directly with the compiler of any given bibliography and, unless otherwise indicated, may assume that the compilers listed have indicated willingness to have their material consulted or duplicated. Ordinarily a copy of any bibliography may be obtained for the actual cost of duplication.

The Research Information Service will welcome corrections or additions to this list and suggestions concerning the further development of a bibliographic exchange.

Acenaphthene:

The Barrett Co., 40 Rector St., New York, N. Y. 174 entries, by author and subject. 1864–date. Abstracts included.

Acrolein:

Preparation and properties. L. H. Flett and J. L. Parsons, Rye, N. H. 100 entries. 1840–1917. French, German, and English literature thoroughly covered.

Adsorption:

Variation of adsorption from solutions with hydrogen-ion concentration. Neal E. Gordon, University of Maryland, College Park, Md. Entries by author, title, and subject. 1909–1921. Abstracts included in some cases. One-half complete.

See also Gas (Baker).

Agricultural Chemistry:

Homer J. Wheeler, 111 Grant Ave., Newton Centre, Mass. 1892–date. Abstracts included.

Air Pollution:

Charles Baskerville. Incomplete.[2] For consultation, write Library, College of the City of New York, New York, N. Y.

Alcohol:

C. C. Stewart, Hanover, N. H. 400 or 500 entries, by author and title. Fairly complete up to 1897. Abstracts included in some cases.

Alcohol, particularly its manufacture and utilization as a motor fuel. E. H. Leslie, University of Michigan, Ann Arbor, Mich. Fairly complete.

Alloys:

Alloy steels and ferro-alloys. Clarence Estes. 4567 entries, classified by elements. For consultation, write Dr. F. B. Dains, University of Kansas, Lawrence, Kan.

Aluminium:

Aluminium and aluminium alloys. Robert J. Anderson, Bureau of Mines, Pittsburgh, Pa. 1000 entries, by author, title, and subject. 1800–1922. 95 per cent complete. In press as a Bureau of Mines publication.

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[1] Dr. H. P. Little has kindly consented to the incorporation into the present list of material of chemical value contained in his list.

[2] Biographies by Dr. Baskerville are incomplete owing to his recent death.

Amalgams:

M. G. Mellon, Department of Chemistry, Purdue University, Lafayette, Ind. 400 entries, by author. 1750–1920.

Amino--phthalic Acid:

See **Phthalic Acid** (Bogert).

Ammonium Nitrate:

Physical and chemical properties. H. W. Baker, Telling-Belle Vernon Co., Research Laboratory, Cleveland, Ohio. 75 entries, classified according to properties. 1837–1918. Abstracts included with tables. Complete survey of English and German abstract journals, with original articles consulted as far as possible. Mimeograph copies obtainable from Dr. C. E. Munroe, National Research Council, Washington, D. C.

Ammonium Sulfate:

Ammonium sulfate as a fertilizer, and its effectiveness in comparison with other nitrogenous fertilizers. M. I. Wolkoff, Agricultural Experiment Station, Urbana, Ill. Fairly complete up to 1919.

Anesthetics:

Anesthetics, ether, chloroform, etc., including all known substances used for anesthesia. Charles Baskerville. To be published in new edition of "Anesthesia" by Baskerville and Gwathmey. For consultation, write to Dr. James T. Gwathmey, 40 East 41st St., New York, N. Y.

Anthocyans:

Andrew Neff, 5520 Blackstone Ave., Chicago, Ill. 120 entries, by author. 1850–1920. Fair from chemical point of view. Copy in University of Chicago Library.

Anthraquinone:

See **Drugs** (Gunton and Okey).

Antimony:

Chemistry, analysis, etc., of antimony. Elton R. Darling, James Millikin University, Decatur, Ill. 2500 to 3000 entries, by author, title, and subject. Nearly complete up to date. Abstracts included in part.

Arsphenamine:

Fulton B. Flick, Iowa State College, Ames, Iowa. 350 entries. Up to March 1921. Very few abstracts included. Quite complete as regards chemistry of the drug, and covers much of application and action.

Asphaltic Cements:

Oxidation of asphaltic cements. H. P. Newton, Georgetown, Ky. Up to 1920.

Autolysis:

Bacterial autolysis. William Shelton Sturges, Cudahy Packing Co., Omaha, Neb. 80 entries by author and title. 1890–1918. Abstracts included. 85 per cent complete. Copy in Yale University Library.

Bagasse:

Use for fuel and paper. Arthur D. Little, Inc., Cambridge, Mass. 32 entries, by author.

Baking Chemistry:

See **Wheat Milling** (Bailey).

Barium Sulfide:

Barium sulfide manufacture and reduction of barium sulfate Engineering Societies Libraries, New York, N. Y. 34 entries. 1898–1918. Abstracts included.

Beet Products:

See **Coloring Matters** (Zerhaw).

Blood:

Analysis of blood. H. A. Mattill, University of Rochester, Rochester, N. Y. 400 entries, by subject. 1917–date. Abstracts included in perhaps half the entries. 75 per cent complete.

Methods for analysis of blood. N. W. Rakestraw, Stanford University, Calif. 400 entries, by author and subject. Up-to-date. Abstracts included in most cases, and will be in all cases when completed. Will be as complete as possible, covering both domestic and foreign literature available. Unavailable at present.

Botany:

See **Pharmaceutical Chemistry** (Arny).

Butyric Acid:

Analysis of butyric acid. Grasselli Chemical Co., Cleveland, Ohio. 24 entries Abstracts included

Calorimetry:

See **Metabolism** (Armsby).

Candelilla Wax:

Arthur D. Little, Inc., Cambridge, Mass. 18 entries, by author.

Cane Products:

See **Coloring Matters** (Zerhaw); **Bagasse** (Little).

Carbon:

Carbon electrodes. *See* **Pitch Coke** (The Barrett Company); **Electrochemistry** (Union Carbide & Carbon Research Laboratories).

Manufacture of carbon black. H. J. Masson, New York University, New York, N. Y. 200 entries, by author. Up-to-date. Complete as possible.

Carbon Monoxide:

Formation of carbon monoxide by burning gas flames. P. A. McCarty. 90 entries. 1870–1917. For consultation, write Department of Chemistry, Ohio State University, Columbus, Ohio.

Casein:

H. Stirling Snell, Grand Haven, Mich. 300 entries, by title. 1869–date. Abstracts included in some cases. Fairly complete, with patent references, 1918–date.

Castor Oil:

Physical and chemical characteristics of castor oil. F. W. Willard, 410 West School Lane, Germantown, Philadelphia, Pa. Entries by author and subject. 1825–1910. Abstracts included in part. 80 per cent complete.

Cement:

Cements involving the sorrel reaction. H. G. Schurecht, Bureau of Mines, Ceramic Experiment Station, Columbus, Ohio. 75 per cent complete.

See also **Asphaltic Cements** (Newton); **Potash** (Western Precipitation Company).

Chemical Education:

Charles Baskerville. Incomplete.[2] For consultation, write Library, College of the City of New York, New York, N. Y.

Chemical Literature:

Card index to chemical literature. Patent Office, Washington, D. C. Contains nearly a million cards and covers the entire field of chemical literature. See House Document No. 1110, 62nd Congress, 3rd Session, Appendix K, pp. 599–618, for description.

Chemical Warfare:

Clarence J. West, National Research Council, Washington, D. C. 1500 entries, by author. Two-thirds complete.

Chemistry:

Charles E. Mullin, care of E. and L. Co., 3rd and Jackson Sts., Camden, N. J. 30,000 entries. 1907–date. Especially strong on textile chemistry and dyeing.

Chemistry and civilization. Charles Baskerville. Incomplete.[2] For consultation, write Library, College of the City of New York, New York, N. Y.

Chemistry and life. Charles Baskerville. Incomplete.[2] For consultation, write Library, College of the City of New York, New York, N. Y.

Chemistry and municipalities. Charles Baskerville. Incomplete.[2] For consultation, write Library, College of the City of New York, New York, N. Y.

See also **Volumetric Chemical Analysis** (Andrews).

Chemists:

Portraits of chemists. F. B. Dains and Clarence J. West. 400 entries, by subject. For consultation, write C. J. West, National Research Council, Washington, D. C.

Chloropicrin:

See **Insecticides and Fungicides.**

Cholesterol:

Cholesterol and fats in their relation to it. Lloyd Arnold, Loyola Medical School, 706 S. Lincoln St., Chicago, Ill. 1500 entries. 1850–1914. Abstracts included. Complete for period covered.

Citric Acid:

Use of citric acid; its salts and esters. The Barrett Co., 40 Rector St., New York, N. Y. 114 entries, by author.

Citrus Fruits:

Citrus fruits and their products. C. P. Wilson, Box 518, Corona, Calif. 250 entries, mostly by subject. 1910–date Abstracts included. 50 per cent complete.

Clay:

Chemical and physical properties, testing, etc., of clay. Clarence J. West, National Research Council, Washington, D. C. 600 entries, by author. One-half complete.

Clays and ceramic arts. J. C. Branner. Additions to "Bibliography of Clays and the Ceramic Arts" published in 1906. Entries by author. For consultation write Division of Geology and Geography, National Research Council, Washington, D. C.

See also **Refractories** (Schurecht).

Coal:

Library of Congress, Washington, D. C. 105 entries, by author. Up to 1920.

Storage of coal. Library of Congress, Washington, D. C. 138 entries, by author. Up to 1920.

See also **Low Temperature Carbonization** (The Barrett Company).

Coal Tar:

Physical constants of coal-tar derivatives. The Barrett Co., 40 Rector St., New York, N. Y. Entries by subject. Figures copied from original source.

Special coal-tar constituents. The Barrett Co., 40 Rector St., New York, N. Y. 80 entries. 1870–date. Abstracts included.

Colloid Chemistry:

Harry N. Holmes, Oberlin College, Oberlin, Ohio. 1500 and more entries. 1870–date. Brief abstracts often included.

Colloids in geology and mining. Thorndike Saville. 89 entries. Very complete to 1917. For consultation, write R. W. Sayles, Harvard University, Cambridge, Mass.

Coloring Matters:

Coloring matters in beet and cane products. F. W. Zerban, Marrero, La. 105 entries, by author. 1890–date. Considered fairly complete.

Combustion Chemistry:

See **Industrial Chemistry** (Strong).

Corrosion:

Corrosion and its prevention. Nathan Van Patten, Massachusetts Institute of Technology. 1300 entries, by author. Up to 1921. Two-thirds complete.

Corrosion of metals. Clarence J. West and Callie Hull. 2000 entries, by author and subject. Three-fourths complete. For consultation, write Division of Research Extension, National Research Council, Washington, D. C.

Corrosion of metals by water and foaming in steam boilers. Marion Hollingsworth. 500 entries. Up to 1915. For consultation write to Prof. C. W. Foulk, Chemistry Department, Ohio State University, Columbus, Ohio.

Cottonseed:

Physiological value and toxicity of cottonseed and some of its products. Icie Gertrude Macy. 150 entries, by author, title, and subject. Up to 1920. For consultation, write Library, Yale University, New Haven, Conn.

Coumarin:

The Barrett Co., 40 Rector St., New York, N. Y. 72 entries, by author and subject. 1884–date. Abstracts included.

Crystallography:

Growth of crystals under pressure. Stephen Taber, Columbia, S. C. 150 entries, by author and title. Incomplete.

Cyclobutane:

Cyclobutane derivatives. L. L. Steele, Bureau of Standards, Washington, D. C. 66 entries. Up to 1914. Abstracts of methods of preparation are included.

Dihydroxybutyric Acids:

J. W. E. Glattfeld, University of Chicago, Chicago, Ill. 26 entries. Up to 1915. Complete.

2,4-Dinitrobenzaldehyde:

Derivatives of 2,4-dinitrobenzaldehyde. Blaine B. Wescott, 1739 Lilac St., Pittsburgh, Pa. (Mt. Olive Station). Up to 1920. Very brief abstracts included. Complete.

Disinfectants:

See **Insecticides and Fungicides; Poisons** (Gray).

Distillation:

Distillation: machinery, process, theory. Edwin M. Baker, University of Michigan, Ann Arbor, Mich. Entries by author and subject. 1907–1919. Abstracts included for more important articles. Does not include patents; otherwise all articles listed in *Chemical Abstracts*.

Fractional distillation. E. H. Leslie, University of Michigan, Ann Arbor, Mich. Fairly complete.

Dolomite:

See **Refractories** (Schurecht).

Drugs:

Anthraquinone drugs, especially *Rhamnus frangula*. J. A. Gunton and Ruth Okey, Transylvania College, Lexington, Ky. 350 entries, by author, title, and date. 1828–1921. Abstracts included for *Rhamnus frangula*. Quite complete.

See also **Arsphenamine** (Flick); **Epinephrine** (Schultz).

Drying:

Drying: machinery, process, theory. Edwin M. Baker, University of Michigan, Ann Arbor, Mich. Entries, by author and subject. 1907–1919. Abstracts included for more important articles. Does not include patents; otherwise all articles listed in *Chemical Abstracts*.

Dyes:

American dye patents. Color Investigation Laboratory, Bureau of Chemistry, Washington, D. C. 3000 patents, cross indexed in seven ways, total cards about 35,000. Indexed under number, intermediates, chemical class, color, application to fiber, fiber on which used and owner. 1861–1921. Abstracts included. Complete to July 1921.

See also **Chemistry** (Mullin); **Coloring Matters** (Zerbaw).

Electric Welding:

James H. Gravell, 1126 S. 11th St., Philadelphia, Pa. 30,000 entries, by patent owner, number and subject. 1840–date. Abstracts included. Complete cross index of welding as disclosed in United States patents.

Electrochemistry:

The battery industry. Union Carbide & Carbon Research Laboratories, Inc., Long Island City, N. Y. 100 entries, by author.

The carbon industry. Union Carbide and Carbon Research Laboratories, Inc., Long Island City, N. Y. 185 entries, by author.

See also **Industrial Chemistry** (Strong); **Pitch Coke** (The Barrett Company).

Enamels:

Enamels, enameling, and enameling raw material. A. D. Landrum, 720 Electric Bldg., Cleveland, Ohio. Entries by author and title, and cross indexed in some cases by subject. Complete to 1918.

Epinephrine:

Adrenalin and adrenalin-like bodies. W. H. Schultz, University of Maryland Medical School, Baltimore, Md. 1500 entries, by author. 1883–1909. Abstracts included in part.

Esters:

Alcoholysis of esters. Jesse E. Minor. For consultation write Dr. Roger F. Brunel, Bryn Mawr College, Bryn Mawr, Pa. Published in part.

Evaporating Apparatus:

See **Heat Transmission** (Badger).

Explosives:

Charles E. Munroe, National Research Council, Washington, D. C. 5000 entries, chronologically by author. 1665–1907. Abstracts included. One-tenth complete.

Extraction:

Extraction: machinery, process, theory. Edwin M. Baker, University of Michigan, Ann Arbor, Mich. Entries by author and subject. 1907–1919. Abstracts included for more important articles. Does not include patents; otherwise all articles listed in *Chemical Abstracts*.

Fats and Oils:

Bleaching of vegetable oils with various earths and blacks. B. H. Thurman, 297 Fourth Ave., New York, N. Y. 1911–1921. 85 per cent complete.

Edible oils and fats. Library of Congress, Washington, D. C. 308 entries, by author. Up to 1918.

Fats and oils. Herbert S. Bailey, Head Laboratory, Southern Cotton Oil Co., Savannah, Ga. 500 entries. 1890–1918. Abstracts included in many instances. Nearly complete.

Fats and oils. George S. Jamieson, Oil, Fat and Wax Laboratory, Bureau of Chemistry, Washington, D. C. 1915–date. Brief abstracts in a few cases. References mostly from *Chemical Abstracts*.

Refining vegetable oils. Charles Baskerville. Incomplete.[1] For consultation, write Library, College of the City of New York, New York, N. Y.

See also **Castor Oil, etc.; Hydrogenation, Viscosity.**

Feldspars:

Physical and chemical nature of the feldspars. Harold L. Alling, University of Rochester, Rochester, N. Y. 107 entries, by author and subject. 1300 chemical analyses.

Ferro-Alloys:

See **Alloys** (Estes).

Filters:

Filters and filtration. J. Edward Porter, Box 785, Syracuse, N. Y. 3000 entries, by author, title, and subject. 1900–1915. Includes patents.

Fireproofing:

See **Waterproofing** (Fenn).

Fish:

See **Piscatorial Chemistry.**

Flax:

Department of Technical Control, American Writing Paper Co., Holyoke, Mass. 163 entries. 1880–1920. Abstracts included. Everything available.

Flesh:

Amino acid distribution of flesh. E. G. Sieveking. 31 entries by author and title. 1899–1922. Abstracts included Fairly complete. For consultation, write C. R. Moulton, 105 Schweitzer Hall, Columbia, Mo.

Nitrogen distribution in flesh (proteins). W. S. Ritchie. 12 entries by author and title. 1900–1922. Abstracts separate but available. Complete, especially with regard to edible flesh. For consultation, write C. R. Moulton, 105 Schweitzer Hall, Columbia, Mo.

See also **Meat.**

Fluorene:

The Barrett Co., 40 Rector St., New York, N. Y. 261 entries, by author and subject. 1867–date. Abstracts included.

Food:

Conservation, production, and economic use of foods. Library of Congress, Washington, D. C. 192 entries, by author. Up to 1917.

Food in relation to health, food rationing, dietetics, etc. Library of Congress, Washington, D. C. 143 entries, by author. Up to 1918.

Fungi:

Physiology of fungi (biochemical). C. U. Frey, 103 W. 183rd St., New York, N. Y. 150 entries, by author and subject. 1880–1916. Abstracts included in some cases.

Fungicides:

See **Insecticides and Fungicides; Poisons** (Gray).

Gas(es):

Gases. M. C. Smith. 12,000 entries, by title, subject, and properties, with attached author list. Few before 1880, since 1900 fairly covered. Brief abstracts and comments in some cases, tabulated data in some, a few critically covered. Everything of probable interest in connection with gas chemistry: physical properties, chemical reactions, manufacture, analysis, commercial application, etc. Conveniently arranged and indexed. For consultation, write Chemistry Section, Bureau of Standards, Washington, D. C.

Diffusion of gases through hot solids. B. Clifford Hendricks, 302 Chemistry Hall, University of Nebraska, Lincoln, Neb. 50 entries, by author, title, and subject. 1863–1920. Abstracts included for practically all references. 75 per cent complete.

Gas absorption: machinery, process, theory. Edwin M. Baker, University of Michigan, Ann Arbor, Mich. Entries by author and subject. 1907–1919. Abstracts included for more important articles. Does not include patents; otherwise all articles listed in *Chemical Abstracts.*

Preparation, chemical, and physical properties of gases. Gas Section, Bureau of Standards, Washington, D. C. 10,000 entries, by author and subject. 1800–date. Short abstracts included in a large number of cases. About complete.

Gelatin:

E. T. Oakes, 85 Ninth Ave., New York, N. Y. 350 entries, by author, title, and subject. Up to date. Abstracts included.

See also Glue (Alexander), (Thiele).

Germanium:

Chemistry of germanium. Frank W. Douglas, Colorado College, Colorado Springs, Colo. Up to 1919.

Gilsonite:

See Petroleum (Carmichael).

Ginger:

Arthur D. Little, Inc., Cambridge, Mass. 20 entries, by author.

Glass:

Alexander Silverman, University of Pittsburgh, Pittsburgh, Pa. 6000 entries, by author and subject. 1822–1914. Practically complete.

See also Sand (Richardson).

Glue:

Glue and gelatin. James Alexander, 255 W. 108th St., New York, N. Y. To appear in an AMERICAN CHEMICAL SOCIETY monograph on this subject.

Glue and gelatin, including testing, chemical and physical methods, complete patent literature, and statistics. L. A. Thiele, Upper-Sandusky or Columbus, Ohio. 2000 entries, including 500 patents, by author and subject. 1814–1920. Abstracts included in part. Very nearly complete.

See also Casein (Snell).

(*To be concluded*)

AMERICAN CONTEMPORARIES

Ira Remsen

IRA REMSEN

REMSEN is most widely known through his textbooks, which have reached every quarter of the globe and have been studied by tens of thousands of students from high school to university. He is best known to the initiated for the long list of researches he has carried out. He will be longest known for the journal which he founded and conducted for thirty-five years, and into which he gathered such a large proportion of American chemical research for that period. He is best loved and most revered by those who have attended his inimitable lectures and have come into close contact with his inspiring personality. More than any other man he typifies American chemistry, for the excellent reason that he has had such a large part in shaping American chemistry.

The founding of Johns Hopkins University in 1876, an institution of an entirely new kind, providing opportunities for advanced study and putting emphasis on research as had not been done before in America, gave a tremendous impetus to higher education. For Remsen it offered a wonderful opportunity, one for which he was peculiarly fitted by his type of mind, his training, his tastes, and his ambitions. He had learned the technic of research from such masters as Liebig, Wöhler, Volhard, and Fittig, but the research spirit he did not have to acquire, for it was that spirit which made him fare forth to a far country to seek the companionship of investigators.

Remsen came into American chemistry during its formative period when his leadership counted for most. Many who were later to mold chemical thought and practice were themselves molded by him. He taught a few hundred; they have taught many thousands. Comparatively few of his students went into commercial chemistry, but a number of these have been prominent figures in some of our largest industries and have carried Remsen's ideals with them. He has never taken out a patent or turned his hand to commercialize any of his discoveries, and has always taught pure chemistry, yet few men have had so great an influence on applied chemistry.

The presidency of the university was thrust upon him to the detriment of chemistry and the violation of his own tastes, but it was desirable that the direction of the university fall into the hands of one who had shared in creating its ideals and who could be trusted to further them. His administration, 1901–1913, was a period of steady progress against difficulties, and was marked by the founding of the school of engineering and the removal of the university to its present splendid location near the edge of the city.

He has served his city, his state, and his country on various commissions, giving his time and strength freely for the public good.

The years since his retirement, in 1913, he has spent in travel, in revising his books, and in giving advice, as requested, to the Government and to several large industries.

Remsen is more than a famous investigator, more than a writer of luminous texts, more than a discriminating editor, more than an inspiring teacher, and more than a university president; he is a real man, interested in life, loving the out-of-doors, full of kindly humor, quick to understand, accessible to all, helpful as a friend, sane in judgment, kindly in estimating others, and scrupulously honest and fair in all his dealings.

He has a way of thinking things through for himself and then going forward, and is not easily turned aside, but never needlessly antagonizes others. Chemists love to honor him and with good reason.

E. EMMET REID

SCIENTIFIC SOCIETIES

Report of the American Delegation to the Third Meeting of the International Union of Pure and Applied Chemistry[1]

The third conference of the International Union of Pure and Applied Chemistry was held at Lyons, France, June 27 to July 2, 1922, under the presidency of Dr. Charles Moureu. The following countries were represented by the number of delegates indicated: Argentine Republic 1, Belgium 4, Brazil 1, Canada 2, Denmark 3, Spain 3, United States 9, France 30, Great Britain 6, Greece 1, Italy 16, Japan 2, Monaco 2, Norway 4, Holland 8, Peru 1, Poland 2, Roumania 3, Switzerland 3, Czechoslovakia 2, Uruguay 1, and Jugoslavia 1.

The United States was represented by the following delegates: Charles L. Parsons, *chairman;* E. W. Washburn, *secretary;* H. S. Washington (represented by alternate John Frazer); R. B. Moore, Edward Bartow, and W. D. Bancroft (represented by alternate Atherton Seidell), members of the Council; A. C. Langmuir, W. A. Noyes, and A. P. Matthews, members of the General Assembly.

Three meetings of the Council and two meetings of the General Assembly were held. The sessions were interspersed with committee meetings, social events, scientific lectures, and numerous excursions to factories in Lyons and vicinity. The visiting delegates and their ladies were royally entertained by the people of Lyons, and the meeting was in every way successful and will long be remembered by everyone present.

At the final session of the General Assembly Sir William Pope was elected president for the ensuing three-year term, and it was voted to hold the next meeting of the Union in the summer of 1923 at Cambridge, England. W. D. Bancroft was elected vice president and member of the executive committee for America. After the adjournment of the conference the delegates were guests of the Lyons committee on a steamboat excursion down the Rhone to Avignon, whence the delegates proceeded by special train to Marseilles where they were the guests of the French Society of Industrial Chemistry at its annual meeting and where they had the opportunity of visiting the very interesting and instructive French Colonial Exposition.

During the meetings the following scientific lectures were given: (1) The Origin of the Synthetic Organic Dyestuff Industry, by Prof. Leo Vignon of the University of Lyons; (2) The Discontinuity of Matter; and (3) The Theory of Radio Chemistry, by Prof. Jean Perrin of the Sorbonne.

ABSTRACTS OF COMMITTEE REPORTS

The following are abstracts of the reports of committees adopted by the General Assembly of the Union:

COMMITTEE ON NATIONAL AND INTERNATIONAL FUEL AND CERAMIC RESEARCH LABORATORIES

The committee made the following recommendations: (1) Each country belonging to the Union shall be invited to formulate through a committee, or other suitable agency, a systematic nomenclature for fuels, covering legal and commercial definitions of the various combustibles, together with an exact description of their various properties, physical, chemical, physico-chemical, and organoleptical. (2) Through the same agency each country shall also make a complete compilation of the methods and apparatus of research, analysis, and testing, which are employed in the country, either officially or by common usage, to the end that this information may be available as a basis of discussion for formulating a set of standard definitions and methods, for international adoption.

In order to facilitate exchange of information, the committee requested that the agency established in each country correspond directly with the president of the International Committee on Fuels.

COMMITTEE ON AN INTERNATIONAL DEFINITION OF THE TERM "CERAMIC"

The committee approved unanimously the recommendations of the American Ceramic Society's committee on this question, and voted that they should serve as a basis for discussion of the question which should be brought before the next meeting of the Union for final consideration, after each country belonging to the Union had had an opportunity to study the report and contribute to the discussion.

COMMITTEE ON REFORM OF NOMENCLATURE

SUBCOMMITTEE FOR INORGANIC CHEMISTRY—The committee recommended that the formula index employed by *Chemical Abstracts* be adopted as soon as convenient by all chemical publications. Other recommendations of the committee dealt with minor points concerning terminology in the different languages.

SUBCOMMITTEE FOR ORGANIC CHEMISTRY—The committee recommended (1) that all questions of nomenclature be submitted for examination and report to the editors of the most important chemical journals; (2) that the functions of the committee be limited to the examination and criticism of the reports received from the editors; and (3) that the committee formulate a report in 1923 comprising a complete system of nomenclature for the adoption of the principal scientific and technical chemical journals and by the authors of dictionaries and didactic works. The General Assembly, in accordance with the recommendations of the committee, appointed Messrs. Greenaway, Marquis and Crane as the committee of editors, and directed that their report should be communicated to the six chairmen of the national committees—*viz.*, Messrs. Angeli, Billmann, Blaise, Norris, Smith, and Votocek—who should examine it within two months after its receipt and transmit it, together with their suggestions, to the secretary of the Union, who in turn would transmit it to the three members of the subcommittee, for formulation of the final report to be presented to the Cambridge meeting of the Union.

SUBCOMMITTEE FOR BIOLOGICAL CHEMISTRY—The preliminary report of Mr. Bertrand was ordered printed and circulated for study in each of the countries belonging to the Union, with the purpose of arriving at final conclusions at the Cambridge meeting.

COMMITTEE ON THE REVISION OF SIGN OF ELECTRODE POTENTIALS

The committee recommended (1) that in referring to the potential of a metal in contact with a solution, the sign of the potential of the metal should be employed; and (2) that when the numerical value of a potential is given, the basis of reference should be indicated, together with all details necessary for its reproduction.

COMMITTEE ON CHEMICAL PERIODICALS

The committee recommended (1) the adoption of the journal abbreviations used by *Chemical Abstracts;* (2) that when titles are in other than Roman characters, a transliteration but not a translation should be employed; and (3) that the abbreviation for the word "Japanese" should be Jpn. and not Jap. The committee also expressed the following views: (1) that central bureaus of documentation and bibliography, in the broadest sense of the terms, be created in the various countries, and that these central bureaus coöperate fully with one another; (2) that there be published a list of the offices of those bureaus which are already functioning; (3) that the decimal system of classification be adopted for the classification of publications of pure and applied chemistry and that all journals publish the appropriate decimal index at the head of each article; (4) that there be established, through coöperation with the Committee of the International Catalog of Scientific Literature, a central register of chemical publications and patents classified by authors; (5) that all chemical publications bear the address of the author or that of the laboratory in which the investigation was carried out; and (6) that all articles published in periodicals be accompanied by an abstract in one of the four languages—English, French, German, or Italian. A temporary committee was appointed to continue the study of the problems of documentation, and in particular to revise the tables of decimal classification for chemistry in coöperation with the International Union of Bibliography.

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[1] Provisional and nonofficial report.

Committee on the International Institute of Chemical Standards

Subcommittee on Physico-Chemical Standards—The committee recommended: (1) that all countries which have not thus far designated a correspondent for the Bureau of Physico-Chemical Standards should be invited to communicate immediately the name of their correspondent to the secretary of the Bureau (University, Rue des Sols, Brussels, Belgium). The secretary of the Bureau was authorized to communicate directly with the different national committees in order to accelerate as much as possible the completion of the lists of these correspondents; (2) that an official representative of the Union be appointed to solicit further financial support for the Bureau on the part of the Belgian industries. (Dr. Emile Mond was appointed as this representative.)

Subcommittee on Pure Products for Research—It was recommended that each member of the subcommittee send to the Secretary General of the Union before the end of April next a report covering for his country the progress which has been made in the standardization of analytical reagents and methods of testing the same. The committee further recommended that for comparative volumetric determination of the halogens in seawater the advisability of employing pure sodium chloride as a standard, in preference to a typical seawater, be studied, owing to the impossibility of controlling exactly the composition of seawater.

Subcommittee on the Documentation of Industrial and Technical Products—This committee made the following recommendations: (1) It is desirable that each of the countries belonging to the Union shall prepare a list of the various industrial chemicals, with an indication of the products actually manufactured in their country in the manner already accomplished in Great Britain and in process of execution in France, these various lists to be later combined in a central bureau at Paris. (2) In addition to the central bureau at Paris there shall be established in each country a corresponding member of that bureau, in order to facilitate the service to be rendered by the bureau to chemists. This representative shall become a depository of all the catalogs and documents published by the central bureau.

Committee on the Establishment of Thermochemical Standards

This committee made the following recommendations: (1) that benzoic acid be adopted as the thermochemical standard for determining the thermal capacity of calorimetric apparatus used for the measurement of the heats of combustion of fuels and organic materials; (2) that standard samples of benzoic acid prepared by the Bureau of Standards of Washington can be obtained from the Bureau of the International Institute of Physical and Chemical Standards at the University of Brussels; (3) that the Union adopt provisionally as the heat of a gram of benzoic acid (weighed in air) the value 6324 cal. 15°; (4) that every author who publishes data on heat of combustion indicate the value used for the heat of combustion of the benzoic acid used for standardizing his calorimeter.

The committee further recommended that the value of the mechanical equivalent of heat should be determined with such precision that the heats of combustion of organic substances and of fuels might be expressed in absolute units.

Committee on the Annual Tables of Constants

This committee adopted the following resolutions: (1) that the Union approve the accounts presented by the Committee on Annual Tables for the year 1921 and that the report of this committee be presented to the International Research Council; (2) that the Union express its appreciation of the great value of this indispensable publication, compliment the International Committee upon the progress made, and approve the program of work recommended for the years 1923 to 1925; (3) that the Union considers it necessary to give to the Committee on Annual Tables the financial support necessary to continue its work, and that it approves the project proposed for an international fund and budget to carry on the work for the next five years; (4) that the Union transmit its recommendations to the International Research Council and that it request the French government to transmit them, through diplomatic channels, to the various countries belonging to the Union or represented on the International Committee on Annual Tables, with the request that these governments communicate them to their scientific academies or national research councils; (5) that the Union express the hope that the scientific organizations and industrial groups in the various countries will act favorably in according the necessary financial support to the work on the tables; that the Union take note of the coöperation established between the Committee on Annual Tables and the Committee on Critical Tables, and compliment the two committees for thus assuring the future of the documentation of physical constants which is so important for the future progress of science and technology, and that the Union further extend to Mr. Marie its thanks for the self-sacrificing efforts which he has made in his work on this committee.

Committee on the Preservation of Food Products

The committee voted to request each of the delegates of the countries represented at the meetings to secure the preparation of a résumé of the work carried on in their respective countries concerning the employment of processes for the conservation of solid and liquid food products, these reports to include an indication of the existing legislation (including importation and exportation) covering the use of preservatives in food products.

Committee on International Patents

This committee devoted considerable time to the discussion of the various aspects of the problem, but presented no recommendations. The work of the committee is to be continued.

Committee on Industrial Hygiene

The committee voted to take up for consideration the problem of industrial fumes.

Committee on Chemical Elements

This committee did not meet at Lyons, owing to the absence of Prof T. W. Richards, but on July 13 a meeting of the committee was held in Paris, with Mr. Georges Urbain presiding. The committee elected Messrs. Baxter, of Harvard University, and Leduc, of France, as additional members. It voted to publish in January 1923 a table of isotopes and of radioactive elements, and that, if a new general table of atomic weights could not be completed previous to that date, the 1922 table should be continued as official for 1923.

. . . . .

The following new officers were elected: president, Sir William Pope; vice presidents, W. D. Bancroft, E. Billmann, E. Paterno, and E. Votocek; secretary general, Jean Gerard. The following countries were admitted to membership in the Union: Australia, Luxemburg, and Peru.

The sessions of the Union were closed with a banquet to all of the delegates by the Chamber of Commerce of Lyons. Mr. Louis Pradel, president of the Chamber of Commerce, presided and toasts were offered by Mr. Leon Bérard, French Minister of Public Instruction, Mr. Herriot, mayor of Lyons, and Mr. Canal, prefect of the Rhone.

C. L. Parsons, *Chairman*
E. W. Washburn, *Secretary*

Bulletin 212 of the South Carolina Agricultural Experiment Station, "Analyses of Commercial Fertilizers," contains the analyses of 722 official samples of commercial fertilizers arranged in the following tables: complete fertilizers (containing ammonia, phosphoric acid, and potash), cottonseed meals, acid with ammonia, acid phosphates, acid with potash, potash salts, materials containing nitrogen only, and miscellaneous. In connection with the tables is a discussion of the results of the analyses, showing wherein some of the samples fell below the guarantee, and a comparison of the yearly average of analyses of the various types of fertilizers from 1891 to 1922. Copies of the bulletin may be obtained from the Agricultural Experiment Station, Clemson College, S. C.

American Electrochemists Invade Montreal

One hundred and ninety-five members and guests gathered in Montreal on September 21 to 23 for the 42nd General Meeting of the American Electrochemical Society. The dual purpose of the organization was clearly emphasized by the lively and interested discussion of well-selected papers on electrochemical subjects, and the opportunity afforded by such a gathering for the promotion of genuine good fellowship among its members. The committees on arrangements provided everything that could be desired, and are to be congratulated on a most successful meeting from every point of view.

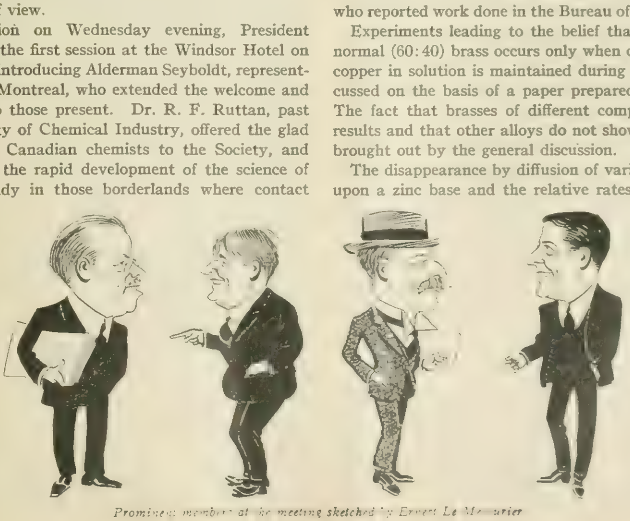
Following registration on Wednesday evening, President Schluederberg opened the first session at the Windsor Hotel on Thursday morning by introducing Alderman Seyboldt, representing Mayor Martin of Montreal, who extended the welcome and freedom of the city to those present. Dr. R. F. Ruttan, past president of the Society of Chemical Industry, offered the glad hand of fellowship of Canadian chemists to the Society, and spoke interestingly of the rapid development of the science of chemistry through study in those borderlands where contact is established with other sciences for the mutual benefit of all. The recent advances in electrochemistry, photochemistry, and other similar fields were dwelt upon, and the advantages accruing to both physics and chemistry from such mutual investigations were pointed out as an earnest of future accomplishment along similar lines. Other papers were devoted in a general way to the subject of electroplating and the properties of electrodeposited metals.

The effect of heat treatment on the properties of electrolytic iron was discussed by Norman B. Pilling. He has found that the initial effect of annealing is a marked hardening of the metal which reaches a maximum at a temperature of 300° to 400° C., and that higher temperatures reduce the hardness to a minimum at a critical point of about 900° C. Microstructural changes and the decomposition of the unstable iron-hydrogen compound in relation to hardness were discussed. A second paper, dealing with alloys of iron with carbon and manganese, prepared *in vacuo* from electrolytic iron, was given by R. P. Neville and J. R. Cain, who reported work done in the Bureau of Standards.

Experiments leading to the belief that the de-zincification of normal (60:40) brass occurs only when contact of the brass with copper in solution is maintained during the corrosion, were discussed on the basis of a paper prepared by Ralph B. Abrams The fact that brasses of different compositions show different results and that other alloys do not show similar properties was brought out by the general discussion.

The disappearance by diffusion of various metals when plated upon a zinc base and the relative rates of diffusion of various metals in this way, as studied in a paper by Walter G. Traub, brought out comments from the Society as to the desirability of first coating the article to be plated with nickel, whose rate of diffusion is notably slow.

The Board of Directors met at luncheon on Thursday to consider routine business and to perfect



Prominent members at the meeting sketched by Ernest Le Messurier plans for the spring meeting in New York. It was found necessary, however, to hold an adjourned meeting after the afternoon session of the Society. The plans for the New York meeting include symposiums on the rarer metals and their applications, under the direction of F. M. Becket, and on electrode potentials under W. G. Horsch. No definite date was fixed for the meeting, pending a decision of the date of the New Haven meeting of the American Chemical Society.

The session of Thursday afternoon was devoted to a symposium on "Industrial Heating." The discussion was started by an interesting study of the broad applications of electrical heating, by E. F. Collins. The changes in resistance of resistance elements and the factors controlling these changes, as brought out in the papers by Hunter and Jones, and by Williams, were intensely interesting in their immediate practical applications.

The address by Dr. A. S. Eve, of McGill University, on "The New Philosophy of Physics," was delivered Thursday evening in the Macdonald Physics Building of the university, to a large and interested audience. Einstein's theory of relativity, the recent investigations and theories of subatomic phenomena, and the effect of these on scientific thought, formed the subject of a most interesting address accompanied by illustrative experiments. An instrument for making visible the bombardment of alpha particles and showing the influence of a magnetic field upon them was seen by many visitors after the lecture.

The electric heating symposium was continued on Friday morning, and special interest was shown in the discussion of electric steam generators, in view of the possibility of their use to balance phases in otherwise unbalanced electric circuits. The insistence of power companies on the use of an equal amount of power from each phase of the circuit is becoming a serious consideration with many consumers, and the belief was expressed that the generation of steam would furnish a satisfactory method of using idle phases.

The papers presented Friday afternoon covered a variety of subjects, including a simple aluminium melting furnace for small charges, the electrolytic oxidation of isoeugenol, the manufacture of carbon bisulfide, the use of the terms, "electrosmosis" and "electrophoresis," preparation of perchlorates by heating chlorates, changes in the resistances of varnishes during drying, especially with reference to electric machinery insulation, and the action of arcs on liquid-insulating compounds.

On Saturday special cars took the party to Shawinigan Falls, where the power plant of the Shawinigan Water and Power Co., the paper plant of the Belgian Industrial Co., and the furnaces of the Canadian Carbide Company were inspected. Luncheon on the lawn of the Cascades Inn filled the short time remaining until it was necessary to take the train back to Montreal.

Calendar of Meetings

Association of Official Agricultural Chemists—38th Annual Convention, Washington, D. C., November 15 to 17, 1922.

American Institute of Chemical Engineers—Richmond, Va., December 7 and 8, 1922.

American Ceramic Society—Annual Meeting, Pittsburgh, Pa., February 12 to 17, 1923.

American Chemical Society—65th Meeting, New Haven, Conn., April 3 to 7, 1923.

Howard N. Potts Medal

At a recent meeting of the Committee on Science and the Arts of The Franklin Institute, an award of the Howard N. Potts Medal was granted to Dr. Charles Raymond Downs and Mr. John Morris Weiss of New York, "in consideration of their notable achievement in the scientific and commercial development for the catalytic vapor-phase oxidation of benzene to maleic acid, and their pioneer work in developing a commercial process for changing aromatic to aliphatic compounds."

Meeting of the British Association for the Advancement of Science

This meeting furnishes about the only opportunity during the year for British scientists to get together; the only other general meetings lasting for more than one day are those of the British Medical Association and the Society of Chemical Industry. Therefore, for other than technical chemists, this is the one opportunity to hear fellow investigators, who reside in different localities, present and discuss papers.

The attendance this year—September 6 to 13, 1922—is reported as about 1800. The meeting is spread over a longer period than are the meetings of the American Chemical Society. Fewer papers are on the program of each section, and more time is allowed for each and for the discussion, which is more extensive than at the meetings of the Society.

In the Chemistry Section, the program for the first session was made up of President Irvine's address and three papers from his laboratory, followed by a vote of thanks to Professor Irvine moved by Sir Edward Thorpe.

The address of Sir William H. Bragg at noon attracted a large crowd. He is evidently one of the bright lights of British science at present. He reviewed the underlying principles employed in studying the structure of crystals, describing the "unit" of crystal structure, which is the smallest particle that still retains the properties of the whole crystal. The number of molecules present in this unit can be determined by X-rays. The dimensions of the crystal unit can be estimated from the relative intensities of the spectra. These data form the basis for interpreting the actual structure of the crystal. He also described some of the newer studies made upon crystals of organic compounds such as tartaric acid.

In the afternoon there was a symposium on photosynthesis, held jointly with the Botany Section. The discussion which followed the papers was quite animated and brought out notable differences of opinion in regard to photosynthesis.

On Friday there was a vitamin symposium before the Physiological and Agricultural Sections. The paper by J. C. Drummond was quite noteworthy. A matter of particular interest is that he has traced the source of vitamin A, contained to such a large degree in cod-liver oil, and has found that the lowest marine plants, the diatoms, contain vitamin A and evidently have the power of synthesizing it. These green plants form the food of plankton, and these in turn are the food of the smaller fish, and these of the larger fish such as the cod, which store this vitamin A in their livers. He has studied the method used in Norway of preparing cod-liver oil for the market, and finds no noteworthy destruction of the vitamins in the process.

HYDROGENATION OF OILS

The paper which appeared to be of most interest on Monday was the hydrogenation paper by E. R. Bolton. The effect of hydrogenation is twofold: (1) to make solid fat from liquid, and (2) to remove impurities. The actual weight of hydrogen involved is small but it occupies a considerable volume, and this introduces difficulties into the process. It is a question whether it is better to transport the oil to the locality where the hydrogen can be best produced, or *vice versa*.

The most important consideration in the life of the catalyst is the purity of the oil treated. The crude oil is reeking with impurities which can be easily removed, and preliminary purification is more economical than rapid destruction of catalyst. The fact that many manufacturers are really purifying their oil by the hydrogenation process and at the expense of the catalyst, instead of by cheaper methods, was pointed out. Nickel is the catalyst universally employed; others cannot compete with it. It is stated that the lower the temperature of reduction of the nickel, the greater the activity of the catalyst, but the more susceptible it is to poisons. Conversely, a catalyst produced at high temperature lasts longer, but acts more slowly in hydrogenation of the oil. In the purification of the oil, the removal of moisture is important. The recovery of the catalyst and reactivation is very costly, and is usually found unprofitable. Bolton and his coworkers have been attempting to develop a catalyst which can be easily recovered and reactivated, and thus form a capital investment of the process, rather than a continual loss. They use nickel wool or fine nickel wire, and activate by first immersing in nitric acid to yield a nickel nitrate coating, ignite in a stream of hydrogen for reduction, and then immediately place under oil to prevent loss of activity until ready for use. The commercial use of this catalyst has not been perfected, but they are using such a catalyst successfully at present for a quick laboratory test of the hydrogenating capacity of given samples of oil. They have found that the rate of poisoning of the catalyst by hydrogen sulfide is inversely proportional to the weight of nickel present, and not a function of the surface of catalyst. They, therefore, think it is better to use a larger proportion of catalyst to oil than others use, especially those who make no attempts to recover catalyst, and therefore charge up so much loss of nickel per ton of hydrogenated oil. They are working on an automatic process involving a device to automatically stop the flow of oil into the apparatus when the catalyst becomes ineffective. This is being operated by change of pressure of the hydrogen resulting from nonabsorption of the gas. The difficulties so far encountered result from hydrogen leaks.

Bolton believes that improvements of this hydrogenation process by engineering skill directed toward more effective stirring, or mechanical aids, are much less effective than work on the chemical features of the process. He thinks that eventually a process will be developed for automatic hydrogenation to a given degree, by simply setting a dial to the figure desired and then starting the process. He has observed that hydrogen under pressure in contact with oil dissolves to a great extent even without stirring. Such oil when drawn off yields up its gas by evolution like carbonated water.

NITROGEN FIXATION

On Tuesday the principal nitrogen paper was read by J. A. Harker, who gave a brief review of the status of each of the three common processes now in use. (1) In describing the *arc* process, he left the impression that on account of its low efficiency, difficulties in connection with cooling and removing nitrogen tetroxide, and possibilities of explosions, this process has no great future in the world's production of fixed nitrogen. The French works based on this process are closed, owing to need of converting the power to other purposes. (2) The *Claude synthetic ammonia* process seemed to have made a favorable impression and the speaker was fairly optimistic of success along this line. (3) The *cyanamide* process is the largest producer of fixed nitrogen and now furnishes it in the cheapest form. Mr. Harker stated that Germany is at present greatly expanding her production by the cyanamide process. He evidently pins more faith to this than to the others. He referred to the development of *Phosphozote*, a combination of cyanamide and phosphate recently made in Switzerland, Italy, and France, and used largely in France. It contains 11 per cent of urea nitrogen and 11 per cent available phosphate. The *cyanide* (*Bucher*) process was claimed to involve excessive costs, and the reactions found to be more complex than was originally supposed. Harker closed with a very powerful warning in regard to Germany's commanding position in regard to nitrogen, and intimated that the provisions of the peace treaty are not being enforced with respect to permitting this enormous development on the part of Germany of excessive supplies of nitrogen for fertilizers and munitions. He said that Germany now produces enough to supply all her needs for agriculture, whereas in 1913 one-half of that consumed by her was imported.

ATHERTON SEIDELL

LONDON

Spring Meeting of American Chemical Society

The final date for the spring meeting of the AMERICAN CHEMICAL SOCIETY at New Haven, Conn., has been set for April 2 to 7, 1923. This date was decided upon jointly by the New Haven and Connecticut Valley Sections of the SOCIETY and the Yale Corporation, and has been approved by the national officers of the SOCIETY. The Yale Corporation has voted to dedicate the new Sterling Chemical Laboratory on Wednesday, April 4.

The Executive Committee, chosen by the two Sections, of which Prof. Treat B. Johnson of Yale University is chairman, has had several meetings, and work is well under way in preparation for the meeting. The following committee chairmen have been chosen:

Program: T. B. JOHNSON
Finance: J. S. GRAVELY
Dedication: JOHN JOHNSTON
Arrangement: A. J. HILL
Registration: BLAIR SAXTON
Hotels and Transportation: RALPH LANGLEY
Smoker: P. T. WALDEN
Reception and Entertainment: C. H. MATTHEWSON
Publicity: W. T. READ
Ladies' Entertainment: MRS. JOHN JOHNSTON

Communications will reach committee chairmen best if sent to A. C. S. Headquarters, Room 157, Sterling Chemical Laboratory, New Haven, Conn.

Chemical Society Meetings, 1922-1923

Rumford Hall, The Chemists' Club, New York City

October 13: Société de Chimie Industrielle.
October 20: Society of Chemical Industry. *Grasselli Medal Award.*
November 10: American Chemical Society. *Joint Meeting* with Society of Chemical Industry, American Electrochemical Society, and Société de Chimie Industrielle.
November 17: American Electrochemical Society.
December 1: Society of Chemical Industry.
December 8: American Chemical Society.
January 5: American Chemical Society.
January 12: Society of Chemical Industry. *Perkin Medal Award.*
February 9: American Electrochemical Society. *Joint Meeting* with Society of Chemical Industry, Société de Chimie Industrielle, and American Chemical Society.
March 9: American Chemical Society. *Nichols Medal Award.*
March 23: Society of Chemical Industry.
April 20: Society of Chemical Industry. *Joint Meeting* with American Electrochemical Society, Société de Chimie Industrielle, and American Chemical Society.
May 4: American Chemical Society.
May 11: Société de Chimie Industrielle. *Joint Meeting* with American Chemical Society, American Electrochemical Society, and Society of Chemical Industry.
May 18: Society of Chemical Industry.
June 8: American Chemical Society.

NOTES AND CORRESPONDENCE

Note on Jell Strength and Viscosity of Gelatin Solutions

Editor of the Journal of Industrial and Engineering Chemistry:

In their very interesting paper on "Jell Strength and Viscosity of Gelatin Solutions," Oakes and Davis [THIS JOURNAL, **14**, (1922), 706] say: "As no data on the 'skin effect' were given by Alexander, this point was investigated." They then give results that show that 16²/₃ per cent solutions of gelatin, when heated to 60° C., allowed to cool (time and all conditions not stated) to 25°–30° C., and then chilled in a thermostat at 21° C., for 16 hrs., did not form a skin that increased the jelly strength. In fact, with a sample that had a chance to form skin they obtained a jelly strength of 490 g., while when skin formation was prevented by toluene, the jelly strength was 500 g.

This shows that under the conditions they used, skin was not a factor, but it is hardly an investigation of the whole point. In testing 25 to 30 per cent solutions of glue at 80° C., especially if the air is dry and the room drafty, a very serious error may be introduced by skin unless precautions are taken to avoid it. I gave no data on skin because it may be avoided by care or provided *ad lib.* by carelessness.

From the results of Oakes and Davis, it seems that two factors are by their variation mainly responsible for the disparities between the viscosity-jelly strength ratios of different gelatins and glues: (1) hydrogen-ion concentration, or effective reaction usually expressed by the pH value, which is Sorensen's logarithmic notation, (2) the ash. Oakes and Davis speak only of the percentage, but the composition of the ash is also of importance, for, as C. R. Smith has shown, calcium exerts a more powerful influence than sodium. This is another instance where we are beginning to recognize the importance of "impurities."

The authors further state: "Since there is probably no gelatin that is not made up of a series of the products of hydrolysis of the original tissue, no gelatin can have what may be called a molecular weight. What is determined is the mean molecular weight of all the various fractions making up the gelatin sample." They then report experiments showing that low-grade gelatins take more acid to bring their pH value from 4.7 to 3.5 than do higher grade gelatins, and believe this indicates a lower molecular weight for the low grades. Unfortunately they fail to report the ash content of the several gelatins used, the importance of which they had just pointed out. Since T. B. Robertson reported that profound hydrolysis does not materially affect the acid-fixing capacity of a gelatin, and since low grades have usually more, and perhaps different, ash from higher grades, it may be that the differences found by Oakes and Davis were in part due to ash.

Oakes and Davis believe that the existence of a maximum at pH 3.5 on the viscosity-pH curve indicates the formation of a (presumably chemical) compound. A. Kuhn[1] has shown, however, as the result of experiments with over fifty aliphatic and aromatic acids, that the swelling of gelatin in acid depends on four factors:

(A) 1—Hydration or simple swelling
(B) 2—Sol formation
3—Hydrolysis
[illegible] 4—Dehydration or salting out

The maximum is reached when the swelling factor is overbalanced by sol formation and hydrolysis. Since viscosity of gelatin is dependent upon the state of swelling or aggregation of its particles, the existence of a viscosity maximum is no proof of the formation of a chemical compound. Kuhn could not decide between that and adsorption. Similarly, the increase in viscosity when acid is added to isoelectric gelatin does not necessarily indicate the formation of a gelatin "salt," as the authors say.

Oakes and Davis, in common with many other authors including J. Loeb, make the mistake of plotting unit differences in pH value by equal increments on the coördinate axes, the result being curves that are logarithmically compressed. In expressing H-ion concentration by Sorensen's convenient symbol, we must remember that it is not an arithmetical but an inverse logarithmic value, deprived of its minus sign, thus:

pH value	Number of times the acidity (or alkalinity) exceeds that of pure water
1	1,000,000
2	100,000
3	10,000
4	1,000
5	100
6	10
7	0[1]
8	10
9	100
10	1,000

[1] Pure water. H- and OH-ion concentration each equal to 10^{-7} mols per liter.

The table also shows that the isoelectric point of gelatin (pH 4.7) represents a very slight acidity. While conductivity water shows pH 7, ordinary distilled water shows pH 5.5 mainly because of absorbed carbon dioxide, and 0.01 *N* hydrochloric acid shows pH 2.02. If logarithmic paper is used then pH values may be plotted, but it is dangerous practice to express results in curves that are logarithmically distorted.

JEROME ALEXANDER

NEW YORK, N. Y.
August 5, 1922

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[1] Kolloidchem. *Beihefte*, 1921.

Some Facts of Interest to the Users of Phthalic Anhydride

Editor of the Journal of Industrial and Engineering Chemistry:

Users of phthalic anhydride who have noted a recent series of advertisements published by the Selden Company of Pittsburgh in various chemical trade journals to the effect that:

> Any person or persons producing, buying or using Phthalic Anhydride of this quality (melting at 130.0° or above) other than that which is produced by The Walker Chemical Company of Pittsburgh, Pa., are infringing on U. S. Patent No. 1,336,132 and lay themselves liable to suit for infringement.

will be interested in a recent ruling by the United States Patent Office which declares, in effect, that the above-mentioned patent[1] is invalid.

That this patent, which claims:

> 1—As an article of manufacture, phthalic anhydride being substantially chemically pure and having a melting point above 130° C. (corrected).
>
> 2—As an article of manufacture, phthalic anhydride in the form of colorless needle-like crystals substantially chemically pure and having a melting point above 130° C. (corrected).

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[1] U. S. Patent No. 1,336,132 was granted to C. E. Andrews of the Selden Company of Pittsburgh on April 6, 1920 (application filed October 14, 1919).

could not be sustained has been evident from the first to those familiar with the facts concerning the history of the preparation and properties of pure phthalic anhydride. Since these have been discussed in detail by Gibbs,[2] and amplified by Bebie,[3] no complete résumé need be given here. That phthalic anhydride substantially chemically pure, and melting above 130° C., is no novelty, is, however, evident from the fact that E. van de Stadt, working in collaboration with Prof. Bakhuis Roozeboom in Amsterdam, prepared and described as early as 1901[4] phthalic anhydride substantially chemically pure and melting at 131.2°. As was mentioned by Gibbs,[2] van de Stadt's investigation has been overlooked by the compilers of the standard treatises on organic chemistry, and I was unaware of its existence at the time of publication of my work carried out in the Color Laboratory of the Bureau of Chemistry.[5]

At the request of the Department of Agriculture, which desired to protect its coöperators on the phthalic anhydride process (of which The Walker Chemical Company was one) from the monopoly which the Selden Company was attempting to create, I filed patent application on the same subject (Serial No. 526,001). This application was drawn in form identical with that of Andrews, but was assigned to the American people. Portions of the ruling of the Patent Office on this application are as follows:

> The Commissioner (of Patents) has refused to declare an interference, under the provisions of Rule 95.

Rule 95 of the Rules of Practice in the United States Patent Office provides, in part, that

> In case the subject matter in controversy has been patented to one of the parties but is deemed by the Examiner not to be patentable, he shall call the case to the attention of the Commissioner, who may direct the declaration of the interference.

The ruling further states:

> The claims are rejected as lacking invention over the article in *Zeitschrift für Physikalische Chemie*, Vol. 41, pages 353, 359 (1902), wherein is shown phthalic anhydride melting at 131.2°.

Presumably the patent examiners were, naturally, unaware of the existence of van de Stadt's investigation at the time of granting of the Andrews' patent, since this article has, as was previously mentioned, been overlooked in the standard treatises. This present ruling by the Patent Office is, however, a clear statement that the article by van de Stadt cited constitutes an anticipation of the subject matter of my application, and since my application was an *exact duplicate* of that of Andrews, this ruling must apply to the latter.

The Selden Company has made another illuminating statement in its advertisements—namely, that

> Phthalic anhydride produced commercially under U. S. Patent No. 1,284,888[6] does not have a melting point of 130.0° Centigrade.

This shows that the Selden Company is not correctly informed on the full development of the Gibbs' process, covered by the patent mentioned. Phthalic anhydride of this degree of purity is produced directly by other coöperators on this work; the conclusion one naturally draws from this statement is that neither the Selden Company nor The Walker Chemical Company has perfected this process to as high a degree as have others.

Finally, two statements made by Andrews,[7] in what purports to be a reply to Gibbs,[2] cannot be permitted to stand uncorrected. Andrews states:

> It can be definitely proved that this original anhydride[8] was a sample of the anhydride produced as described in the patent under discussion (U. S. Patent 1,336,182) and sent to the Color Investigation Laboratory of the Bureau of Chemistry for investigational purposes.

and

> It has been shown that Monroe carried out his work with material made according to U. S. Patent 1,336,182, which is the one under discussion.

The conclusion one naturally draws from these bald statements, namely, that the material used in my work was the exclusive product of The Walker Chemical Company, is entirely false. The anhydride used in this work included samples of the products of two coöperators on the air-oxidation process (of which The Walker Chemical Company was one) and of one firm using a chromic acid oxidation process. Perhaps the most charitable assumption in regard to these very singular statements of Mr. Andrews is the unlikely one that he was unaware of the coöperation of other firms than The Walker Chemical Company.

Kenneth P. Monroe

Penns Grove, N. J
June 21, 1922

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[2] This Journal, **12** (1920), 1017.

[3] *Ibid.*, **13** (1921), 91.

[4] "Barnsteenzuuranhydride En Phthaalzuuranhydride in hun gedrag tegenover water," Dissertation, Amsterdam, J. H. de Bussy, **1901**. "Bernsteinsäure-und Phthalsäure-anhydrid in ihrem Verhalten gegenüber Wasser," *Z. physik. Chem.*, **41** (1902), 353.

[5] This Journal, **11** (1919), 1116.

[6] U. S. Patent 1,284,888. "Process for Manufacturing Phthalic Anhydride, Phthalic Acid, Benzoic Acid and Naphthaquinone." H. D. Gibbs and C. Conover. Issued November 12, 1918.

[7] This Journal, **13** (1921), 167.

[8] The anhydride which was the source of the purified material used in my work in the Color Laboratory of the Bureau of Chemistry.

Bibliography and Research

Editor of the Journal of Industrial and Engineering Chemistry:

The August 25, 1922, issue of *Science* contains an article on "The Record of Science," by W. W. Bishop, librarian of the University of Michigan. The text chosen for this article is, "Bibliography is the *foundation* of research." This statement could not come from any man better qualified to know the value of bibliographical aid in research. Mr. Bishop points out the increasing tendency of the present time to depend more upon the records of laboratory observation than upon the records of science to further our research work.

A comparison of the amount of funds spent in research fellowships and funds specially devoted to research laboratories, with the amounts spent in, or on, the book sciences, bears out Mr. Bishop's statement that present-day research investigations are carried on on the basis of observation in the laboratory, with little or no regard for the records of science.

An examination of the revised edition of "Research Laboratories in Industrial Establishments in the United States," published by the National Research Council in 1921, shows that there are 526 institutions with research staffs and laboratories for investigations in the physical and chemical sciences, and the list of the amounts spent on research shows that there are 565 funds available for research in all branches of the science except the "book sciences." These 565 funds are reported to yield annually, in round numbers, over $22,000,000. In neither publication is there any mention made of funds or laboratories in the "book sciences." Yet bibliography is the *foundation* of research!

Perhaps the most signal attempt at arriving at a "drive" for endowments for laboratories of "book sciences," is the work of the Pittsburgh Section of the American Chemical Society. The energies of this body of men, working for a period of several months, finally amounted, in dollars and cents, to $2500. The September issue of This Journal reported, in an article on the industries of Pittsburgh, that the industrial capital invested in the Pittsburgh District amounted to $3000,000,000. If bibliography is the *foundation* of research, and real thinkers tell us it is, research in the "Workshop of the World" must be on a pretty poor foundation, if $2,500 is the sum forthcoming from an area representing invested capital of $3,000,000,000.

If Pittsburgh stood alone on its poor foundation for research, we might let the fact pass by unnoticed. It has a lot of company throughout the United States.

An extract from Principal Irvine's address before the British Association for the Advancement of Science in June shows that across the sea a similar idea is gaining impetus.

> Among the more *specific* problems which confront this Board are the following:
>
> 1—The creation of research libraries where reference works can be consulted immediately.
>
> 2—The provision of publication grants, so that where no periodical literature is available the work will not remain buried or obscure.
>
> 3—The allocation of traveling grants to enable workers to visit libraries, to inspect manufacturing processes, and to attend the meetings of scientific societies.

Now if an Englishman, who is rarely further away from London or Paris than a few hours' train ride, with the wonderful resources available at either place, thinks that it is advisable, in the interest of research, to suggest "the allocation of traveling grants to enable workers to visit libraries," then there must be something in the statement that "bibliography is the foundation of research"—yet Americans several days away from New York, Chicago, or Washington, still prefer either to depend upon the mail or do without.

Why not, then, arouse sentiment in the industrial world for furthering the establishment of endowments for laboratories of "book sciences" and fellowships in bibliographical work, or—as I choose to term it—research "fact-oring," for bibliographical work is searching for facts?

K. C. WALKER

PITTSBURGH, PA.
September 27, 1922

Present Practice of Dynamite and Chemically Pure Glycerol Distillation—Correction

Footnote one in the article under the title above [THIS JOURNAL, **14** (1922), 487] should be corrected to read:

"Patent pending, Serial No. 450,998, William Garrigue & Company."

PARIS LETTER

By CHARLES LORMAND, 4 Avenue de l'Observatoire, Paris, France

The French chemical industry is slowly returning to normal conditions. Nevertheless, it is still having difficulties because of the high rates on the French railroads for the transportation of raw materials.

In factories of such large chemical industries as the manufacture of sulfuric acid and of superphosphates, about 50,000 tons of raw materials are necessary, a large part of which consists of pyrites, phosphates from Tunis, and coal, which has to come from the port to the factory by railroad. The cost of transportation of these raw materials is about 30 per cent of the amount of the factory business, even exceeding the salaries of the officials.

These rates are imposed by the railroad companies in order to meet their financial obligations, but they are heavily burdening all the industries, especially the chemical industry. Some of these are already thinking of moving their factories from the interior near to the ports where the raw materials arrive, thus putting upon the buyers the cost of transportation of the finished products.

POTASH

It was recently announced in France that the committee of the two Houses at Washington had decided to strike off the duty on potash. This decision must have been taken following the announcement that an agreement had been made between the French and German potash societies. We have already written concerning the preliminary conferences for the purpose of such an agreement, which has not yet been completed.

In 1919, the producers of German potash thought they would have to compete with the French producers in Alsace, and because the capacity for production in the German basin is greater than in the one in Alsace, the German industries tried to form a trust with the Alsatian producers, in which the latter would have only a 10 per cent interest. We have already spoken of the efforts made by Alsatian producers to increase their production so as to be formidable rivals of the German producers. The latter, in view of these efforts, began a competition in price which the Alsatians were able to combat, in spite of the depreciation of the mark.

The German producers are considering two solutions—either an alliance with Alsatian producers, or competition which, because of the exchange, will lead to the destruction of the Alsatian industry. The first solution is possible only if the French government approves, when the exploitation of mines project is discussed in Parliament.

The present price of German potassium chloride is 132 fr. 30 a ton, while the Alsatian chloride is about 450 fr. per ton. This large difference in price gives the German potash an advantage in exporting.

PYREX GLASS

The American Chemical Warfare Service in France, with its well-equipped laboratories, began to extend the use of pyrex glass in our country. A French society has, since 1919, had the exclusive selling rights of this American glass. In view of this increase in consumption, this society has decided to construct in France a factory to make pyrex glass for laboratories and industry. This factory will be erected in the vicinity of Nemours in the Fontainebleau region, where an abundance of the silica sand necessary for the manufacture of this glass is found.

PURE CHEMISTRY

The purely chemical accomplishments have not been many during the vacation months. I have told you of Messrs. Français and Blanc, who have succeeded in obtaining iodobismuthate of alkaloids and basic nitrates—aniline, pyridine, quinoline, theobromine, caffeine, morphine, codeine, quinine, atropine, arecoline, sparteine. These iodobismuthates have been crystallized and make possible the isolation of these alkaloids.

M. Gabriel Bertrand, who in 1912 at the Congress of Applied Chemistry in the United States communicated his investigations on the role of the infinitely small in agriculture, especially of manganese, is continuing research along this line. He has shown the presence of cobalt and nickel in vegetables. The quantities of cobalt found in the vegetable kingdom vary from 0.005 mg. to 0.3 mg. per kg. of plants. The cobalt has been found to be in the form of cobalt nitrite.

The nickel found in the vegetable kingdom varies in amounts between 0.01 mg. and 2 mg. per kg. This has been isolated in the form of dimethylglyoxime and of sulfide.

September 29, 1922

A committee of the Salesmen's Association of the American Chemical Industry, of which Williams Haynes of *Drug & Chemical Markets* is chairman, is actively investigating the relative merits of the various plans suggested for the Chemical Exposition and has sent a questionnaire to all exhibitors in the hope of reaching a satisfactory conclusion on the matter.

For some time there has been on the market a noninflammable motion picture film made of acetate cellulose instead of the usual nitrocellulose or celluloid. Because of the many dangers incurred with inflammable films, France has passed a law whereby all films used after June 1925 must be of noninflammable stock.

WASHINGTON NOTES

DR. STRATTON RESIGNS

By the resignation of Dr. S. W. Stratton as Director of the Bureau of Standards to accept the presidency of the Massachusetts Institute of Technology we are again very forcibly reminded of the miserably poor salaries the Government pays its employees and especially its scientific workers. Secretary Hoover in announcing the resignation of Dr. Stratton commented as follows:

> The loss of Dr. Stratton as head of the Bureau of Standards is a real national loss. He has built up that service from a bureau devoted to scientific determination of weights and measurements to a great physical laboratory coöperating with American industry and commerce in the solution of many problems of enormous value to industry, which the commercial laboratories of the country, from lack of equipment and personnel, have been unable to undertake.
>
> While the Massachusetts Institute of Technology is to be congratulated on securing Dr. Stratton, one cannot overlook the fact that the desperately poor pay which our Government gives to great experts makes it impossible for us to retain men capable of performing the great responsibilities that are placed upon them.
>
> The Massachusetts Institute of Technology, an educational institution, finds no difficulty in paying a man of Dr. Stratton's caliber three times the salary the Government is able to pay him.
>
> Dr. Stratton has repeatedly refused large offers before, but the inability of the scientific men in the Government to properly support themselves and their families under the living conditions in Washington, and to make any provision for old age, makes it impossible for any responsible department head to secure such men for public service at government salaries.

It is hoped that a few such illustrations as the present one will wake Congress up to the seriousness of the situation and to a realization of the necessity of paying to the scientific workers in the Government salaries that can at least compare favorably with those paid on the outside.

No announcement has yet been made as to Dr. Stratton's successor, but rumors are rife and many speculations are afloat regarding the future Director of the Bureau of Standards. Dr. Stratton, however, will not take up his new duties until January 1 and it is believed that the field will be thoroughly canvassed before his successor is appointed. Because of Secretary Hoover's well-known policy of promotion within the service there are those who think he will recommend to the President the appointment of someone at present in the Bureau of Standards.

A VISIT FROM ENGLAND

Mr. F. E. Hamer, Editor of *Chemical Age* (*London*), spent three days in Washington visiting the various points of interest in and around the city. He seemed particularly interested in his visits to the government laboratories, and expressed himself as well pleased with the progress being made in this country, both in government and in industrial organizations. On Monday evening, October 16, Dr. Charles L. Parsons, Secretary of the SOCIETY, and Mr. H. E. Howe, Editor of THIS JOURNAL, gave a dinner in his honor at the Cosmos Club. Those present to meet him were:

W. D. Bigelow, Chief Chemist, National Canners Association
W. M. Clarke, Chief Chemist, Hygienic Laboratory, Public Health Service
F. G. Cottrell, Director, Fixed Nitrogen Laboratory
Amos A. Fries, Chief, Chemical Warfare Service
C. R. DeLong, Chief, Chemical Division, Department of Commerce
F. S. Dickson, Director, Chemical Division, Treasury Department
W. F. Hillebrand, Chief Chemist, Bureau of Standards
W. F. Keohan, Washington Representative, Chemical Foundation
H. C. Parmelee, Editor, *Chemical and Metallurgical Engineering*
L. I. Shaw, Assistant Chief Chemist, Bureau of Mines
E. E. Slosson, Director, Science Service
E. W. Washburn, Editor, International Critical Tables, National Research Council

He came to this country primarily as the representative of Benn Brothers, Ltd., to attend the sessions of the Associated Business Papers, Inc., and the National Conference of Business Paper Editors. He takes back to England with him impressions and information concerning things chemical in America that he could not possibly have obtained in any other way, and he has left with us a much better understanding of the problems confronting our English cousins. Since our two countries are one in working for the progress of mankind we believe that such interchange of ideas as has taken place during the visit of Mr. Hamer will go far toward cementing the good feeling existing between the two countries.

We are glad to have had this visit from him and hope it will be repeated in the near future.

NEW TARIFF RULES

The Tariff Commission is making every effort to expedite its work in drafting rules and regulations for the administration of the flexible section of the new tariff law, realizing as it does the vital interest that the various industries, importers, and the country generally, have in this matter. In framing these regulations the chief object in the minds of the commissioners is fairness to all. With this in view it is stated that the regulations will be so drafted as to discourage mass presentation of applications for changes and thus make it plain that a complaint from a single individual, partnership, or corporation will have as much weight with the commission as that from an entire trade or business organization. Furthermore, the Commission is planning complete publicity for all proceedings from their inception to their conclusion.

NEW RULES FOR ENTRY OF DYES

Close on the heels of the announcement that the President will very probably call an extra session of Congress in November comes the statement that importers of dyestuffs are preparing to attack the rates in the new tariff law. Meantime the Treasury Department is coöperating with the Bureau of Standards for the purpose of formulating a set of standards for the appraisal of dyes. This will necessarily involve considerable laboratory work, and much careful study and consideration, so that it will probably be at least several months before the standards are promulgated.

Customs officials are also busily engaged in drawing up rules for the guidance of importers in entering dyes, and are striving in every way possible to coöperate with importers in facilitating the entry of their goods. The law presents many new and complicated problems, however, and under the most favorable conditions but slow progress can be made.

RENEWAL OF ALABAMA POWER COMPANY LEASE

Secretary Weeks has renewed the lease of the Alabama Power Company for the operation of the Government's steam plant at Muscle Shoals for another year. This renewal has no direct bearing, however, on the offers that have been made by Henry Ford and others for the purchase of the plant, since under the terms of the contract it may be canceled on thirty days' notice. This step was taken because, in the opinion of Secretary Weeks, certain mills and other industries would otherwise be compelled to close down or curtail operations.

FOOD STANDARDS COMMITTEE MEETS

At a meeting of the Food Standards Committee, held in Washington on September 25 to 29, certain changes in the standards for cayenne and oil of cassia were adopted, and the definitions and standards for cacao products and breads modified to conform to the evidence obtained since the publication of the tentative definitions and standards for these products. The committee also revised its definitions and standards for condensed milk, evaporated milk, concentrated milk, butter, renovated butter, ginger-ale flavor, ginger ale, cacao products, edible vegetable oils and fats, breads, and condiments (spices and flavoring extracts).

NEW LABORATORY ESTABLISHED IN THE BUREAU OF CHEMISTRY

A laboratory of crop chemistry to supersede the plant chemical laboratory has been established in the Bureau of Chemistry. Dr. Edgar T. Wherry has been placed in charge with Dr. Jehiel Davidson as assistant chemist. This laboratory will continue and expand the work formerly done in the plant chemical laboratory, the general field of investigation being the influence of environment on the chemical composition of crops. Dr. Davidson will continue his studies of the composition of the crop as influenced by the time of application of fertilizer.

October 17, 1922

Personals

Dr. Frank S. Washburn, president of the American Cyanamid Co., New York, N. Y., died on October 9, 1922.

Mr. F. H. Chamberlain, formerly president of the Heyden Chemical Company of America, is now president of the National Sponge & Chamois Co., New York, N. Y. This change followed the purchase of a majority interest in the Heyden Chemical Company by B. R. Armour of American Aniline Products, Inc.

Mr. E. W. McCullough has resigned his position as director of the Division of Mining and Metallurgy, Republic Creosoting Co., to accept an appointment as consulting engineer for refuse disposal with the Indianapolis Sanitary Commission, Indianapolis, Ind. The work will involve the design and construction of a new plant.

Mr. George H. Rhodes has resigned as assistant in the Chemistry Department of the Massachusetts Institute of Technology, Cambridge, Mass., to accept a position in the Color Laboratory of Cheney Brothers, South Manchester, Conn.

Dr. Charles S. Venable has resigned as assistant director of the Research Laboratory of Applied Chemistry of the Massachusetts Institute of Technology to become director of research for the Viscose Company at Marcus Hook, Pa.

Mr. M. M. Austin has resigned his position as chemist in the research laboratory of the National Malleable Castings Co. to join the teaching staff of the Division of Industrial Chemistry at the University of Illinois.

Mrs. Lillian Segal Kopeloff is now in charge of the newly established Research Department of Biological Chemistry at the Psychiatric Institute of the New York State Hospitals, Ward's Island, New York, N. Y.

Mr. Eric R. Jatte, who recently completed his work for the Ph.D. degree at Columbia University, has gone to Stockholm for a year of study. He holds an American-Scandinavian fellowship for the year 1922–1923.

Dr. Ralph T. Goodwin, who took his degree in 1922 in the Department of Chemical Engineering at Columbia University, has been appointed to a position in the research department of the Standard Oil Company of New Jersey. Dr. Goodwin will have as his special concern the shale oil interests of the company.

Mr. Edward O. Dunkley, who from 1913 to 1922 was chief metallurgical chemist at the Panama Canal, has become associated with the Kober Chemical Company, Inc., Hastings-on-Hudson, N. Y., as chemist. His present work is in connection with the production on a commercial basis of arsphenamines, mercurials, and ultrafiltration processes.

The following have joined the staff of the Research Laboratory of the Eastman Kodak Company: **Helge Schibsted**, formerly with the Atmospheric Nitrogen Company; **Clyde Brockett**, Massachusetts Institute of Technology, 1922; **Alasco Burgess**, Bates College, 1922; **D. Henry Harris**, Massachusetts Institute of Technology, 1922; and **Roger P. Loveland**, Grinnell College, 1919.

At the inauguration of **Dr. Charles R. Richards** as president of Lehigh University, the degree of Doctor of Science was conferred upon **Walter S. Landis**, chief technologist of the American Cyanamid Co., New York, and **Harlan S. Miner**, chief chemist of the Welsbach Light Co., Gloucester, N. J. Both Dr. Landis and Dr. Miner are alumni of Lehigh University.

Mr. C. C. Concannon has been appointed assistant chief of the new Chemical Division of the Department of Commerce. For about five years Mr. Concannon was associated with Takamine, Inc. He is thoroughly experienced in the exportation of chemical products to foreign markets and is a valuable addition to the staff of the Division.

Dr. Leon W. Parsons has resigned as assistant director of the Research Laboratory of Applied Chemistry of the Massachusetts Institute of Technology to accept a position as chief chemist of the Tidewater Oil Co., Bayonne, N. J.

Mr. John V. N. Dorr has recently returned to New York after a six months' trip to England, France, and Germany, made for the purpose of a closer acquaintance with the numerous installations of Dorr methods in the metallurgical and chemical plants of those countries. Mr. Dorr found considerable industrial depression in England, and was impressed with the spirit of hard work which is evident throughout Germany.

Industrials

On September 6, 1922, the old chemical laboratory of the Massachusetts Agricultural College was destroyed by fire. During the last legislature a new laboratory was provided for by an appropriation of $300,000, and it is expected that the building will be ready for occupancy in August 1923.

Chemists interested in the sampling and analysis of pig iron will find the booklet "Methods of the Chemists of the United States Steel Corporation for the Sampling and Analysis of Pig Iron" of great assistance. The booklet has recently been issued to take the place of one of a similar title published by the Carnegie Steel Company in 1912. A committee chosen from the chemists employed by the various subsidiary companies of the United States Steel Corporation rewrote the booklet, giving full consideration to recommendations concerning improved methods and operations which were requested from the chemists of the various works.

The Province of Quebec has purchased from the U. S. Radium Corporation one gram of radium for the use of its citizens in the treatment of cancer and other malignant diseases. The radium will be sent to the University of Montreal, where, under the supervision of Dr. J. A. Gendreau, it will be at the service of the people of the Province.

Engineers in the employ of Henry Ford are reported to have been for several months surveying the Wisconsin and Kickapoo Rivers to ascertain their possibilities for water power. The object is to develop an electricity plant with a view to establishing a zinc oxide plant for the manufacture of zinc for auto tires.

The Brown Instrument Company has opened a New England branch, with offices at 185 Devonshire St., Boston, Mass., in charge of Mr. George Goodman.

The F. S. Pearson Engineering Corp., New York, N. Y., has reëstablished its department for Industrial Management and Technical Auditing of Industries and Public Utilities, which will be carried on together with the usual work of financing, developing, design, and construction of engineering projects and industrial plants.

The B. F. Sturtevant Company has recently issued a bulletin describing construction and uses of its unit driers.

The Duriron Co., Dayton, O., has opened an office in Buffalo, N. Y., in charge of Mr. N. E. Philpot, who for the past two years has been engineer in charge of the company's Cleveland office.

A series of leaflets on freight traffic service has been prepared by the Frederick A. Kirk Co., New York, for the purpose of furnishing information on various questions in connection with traffic matters. The leaflets cover rates, routing, classification, demurrage, export shipments, claims, and expediting. Copies may be obtained from the company.

Twenty-three companies, representing 85 per cent of the pottery industry of the United States, and twenty-four officers of these companies, have been indicted on the charge of conspiring to fix prices and unlawfully restrict sales. This indictment is the last of the series resulting from the housing investigation of the Lockwood committee, authorized by the New York State Legislature. The defendants are specifically charged with engaging in a price-fixing combination whereby they refrained from competing with each other, on a price basis, thus exacting "uniform, arbitrary and noncompetitive prices," and are also charged with being barred by common consent from selling their products directly to builders, architects, or contractors.

The German dye cartel has again doubled its capital stock, issuing about 6,000,000,000 marks of new stock. The new issue has been acquired by a consortium of German banks, which has also taken over all the junior stock of the Badische Anilin- und Sodafabrik (worth about 40,000,000 marks, at 650 per cent above par), which was issued for the purpose of reconstructing the Oppau factories blown up last year. Chemical stocks jumped more than 1000 per cent following the announcement of the capital stock increases. The rise was also attributed partly to individual purchases of German dye stocks by Americans, in the belief that the new American tariff was not unfavorable to the German dye industry. An especially big demand for the stock of the Badische Company is reported because of the plans of the company to exploit the inventions of Dr. Schweitzer, which it is claimed will utilize low-grade products in the manufacture of high-grade fabrics.

BOOK REVIEWS

Principles of Leather Manufacture. By H. R. Procter. 688 pp. 2nd edition. D. Van Nostrand Co., New York, 1922. Price, $10.00.

Procter's "Principles of Leather Manufacture" has been the standard text in the English language since it appeared in 1903. The essential changes in the second edition consist in the rewriting of the chapter on The Chemistry of Hide and the addition of five new chapters: Physical Chemistry of Leather Manufacture; The Colloid State; Pickling and Depickling; Japanned and Enameled Leathers; and Conclusion; with the author's "Original Papers on the Gelatin Equilibrium," an article by Atkins and Thompson on "The Determination and Control of Acidity in Tan Liquors," and another by Atkin and Atkin on "The Caustic Alkalinity of Lime Liquors" as appendices.

The portions of the book devoted to the chemistry and physics of the subject have been materially revised to include the more modern conceptions. The new chapters are all good, and those on Physical Chemistry of Leather Manufacture and on The Colloid State particularly should appeal to the practical mind since they give more recent conceptions concerning the foundations of tanning in Procter's inimitable clear style, a style which physical chemists in general might well adopt.

The revision of the chapters on the actual operations and processes of tanning consists chiefly of short insertions or additions which bring the subject up to date and give useful practical information in pithy form. Several of the chapters remain almost entirely as in the first edition, others are materially improved. While there are additions to the chapter on vegetable tanning materials, the original figures for tannin content unfortunately stand in all cases. The statements concerning the tanning materials of the United States show an unwarranted ignorance of the subject. Hemlock and oak barks are dismissed in short paragraphs, the illustration of the leaves and acorn of chestnut oak (*Q. prinus*) is erroneous, as it was in the first edition. American chestnut, the most important native American tanning material, is not even mentioned, nor are the oaks, hemlocks, and other tanning materials of the Pacific Coast. The tannin content of American sumacs (*R. glabra*, *R. typhina*, *R. copallina*) is stated, as in the first edition, to be 10 to 25 per cent, while actually it is from 20 to 30 per cent. One page is devoted to saw palmetto and three to canaigre. Saw palmetto is but little used, and canaigre not at all.

The new chapter on japanned and enameled leathers is confessedly very general, since the processes are even yet more or less secret. It seems, however, that this chapter could have been brought more nearly up to date.

The conclusion is an excellent, informing, and stimulating brief summary of the recent researches in the field of tanning chemistry. However, the reviewer confesses to a strong prejudice against the interchangeable use of the words "tanning" and "tannage," believing that the latter is only properly used to designate "kind" as oak, chrome tannage, etc.

The book is particularly free from typographical errors, the only ones of importance noted being T. H. Moran for T. H. Norton, and *J. Am. Leather Chem. Assoc.*, **14** for **13** (p. 307).

The book weighs 4.1 pounds. It is well printed on a thick heavy paper. The thickness and weight could well be 40 per cent less. May the time soon come when publishers will give more consideration to the convenience of the reader in these particulars. It is not necessary to make a book heavy and unwieldy in order to sell it.

F. P. Veitch

World Metric Standardization: An Urgent Issue. Compiled by Aubrey Drury. 2 × 15 cm., 525 pp. Published by the World Metric Standardization Council, San Francisco, Calif. Price, cloth, postpaid, $5.00.

Too long the advent of world metric standardization has been left to chance, and it is fortunate that public-spirited individuals have been willing to spend the time and effort necessary to correlate the movement in the United States and Great Britain making toward world standardization. Continental countries are working out far-reaching programs of standardization in the building up of an unprecedented industrial structure to be used in world trade. All the new countries resulting from the war have adopted the metric standards, and in 1921 both Japan and Russia accepted them, leaving Great Britain and ourselves the only nations not formally committed to their gradual adoption.

It will be a surprise and an inspiration to many to learn how much is being done in these Anglo-Saxon countries. Hundreds of organizations are on record as in favor of the advance. The opinions are given here of prominent men in every walk of life; manufacturers, merchants, engineers, officers, scientists, physicians, lawyers, clergymen, editors, etc. This book also contains a lengthy bibliography of pro-metric literature.

Some have been misled into believing that the adoption of the metric system will immediately involve great changes in the products of manufacturing and not merely in the designations of those products. In the chapter on the cost of metric standardization, the Britten-Ladd Bill, recently before Congress, is given in full, and it is emphasized that the change is compulsory only in *merchandising*. The change will be gradual, and instead of a loss it is estimated that there will be a positive gain far outweighing the cost, even during the transition period. When these benefits are appreciated, the use of metric standards in manufacturing will be rapid and the present unreasoning opposition will disappear. The opposition, of course, denies that gradual introduction is practicable, but this contention is flatly contradicted by the experience of the Waltham Watch Co., the De Laval Separator Co., The Goodyear Tire and Rubber Co., and the Baldwin Locomotive Works, who use metrics in manufacture without difficulty.

Eugene C. Bingham

Chemicals and Industrial Materials with Their Commercial Uses. Compiled and published by Charles Argles, 39 Corporation St., Birmingham, England. Price, 10/6 net.

This book consists of 20 lists of chemicals and other materials. The first list contains nearly 700 names of chemicals in alphabetical order, each followed by a list of industries or processes in which the chemical is used. The uses are arranged without reference to alphabetical order or relative importance. No descriptions of the chemicals are given, and no cross references to indicate that names like calcium carbonate, lime carbonate, and chalk may refer to similar substances.

A few bits of information from the first part of the book show its general character.

> Calcium oxide is used for glass manufacture, leather industry, building trade, metallurgy, rubber industry, and paper manufacture. Lime is not used in metallurgy or in paper making, but is used for the four other purposes for which calcium oxide is used. In addition lime has 12 other uses which include the production of calcium salts, the manufacture of chemical products, the production of caustic soda and the manufacture of bleaching

powder. Alkali has 12 uses, caustic soda 15, soda hydroxide 9, and sodium hydrate 1. Other chemicals and the number of uses for each are: black mustard 3, dried blood 1, ox gall 3, suint 2.

The second list contains over 400 names of industrial materials, presumably not chemicals, with the uses of each. A few items and the numbers of uses are: aniline salt 1, brimstone 7, corn oil 4, maize oil 8, corn weevils 1, coumarin 2, fuchsine 2, lard 7, lye 2, macaroni 4, dried milk 1, milk of lime 6, milk powder 3, quicklime 2, rags 4, saccharin 6, sand 4, treacle 7, vanillin 4.

Eighteen other lists give materials used in the following industries: agriculture, baking and confectionery trades, brewing trade, dyeing and calico printing, glass trade, manufacture of inks, leather and tanning trade, paint and varnish trade, paper making, perfumery trade, photography, process engraving and lithographic trades, manufacture of rubber and rubber articles, soap trade, manufacture of sweetmeats, textile trade, preparation of vegetarian foods. These lists contain a few names of substances not given in the first or second lists, such as sodium hydroxide, potassium caustic, potassium hydrate or hydroxide.

Since the publication is an index the absence of page numbers causes no inconvenience. The statement in the preface, "The uses of raw materials, as applied to various trades, have not (as far as I know) been hitherto published," indicates that the author did not have a copy of the Condensed Chemical Dictionary, published by the Chemical Catalog Company. A copy of the dictionary would have saved some of the "no small trouble and difficulty" involved in his compilation. The book is privately printed.

W. D. Collins

Technical Records of Explosives Supply, 1915-1918. VII—Manufacture of Nitric Acid from Niter and Sulfuric Acid.

86 pp., 33 figures. Ministry of Munitions and Department of Scientific and Industrial Research, London. H. M. Stationery Office. 1922. Price, 11s.

During the war the production of nitric acid from sodium nitrate and sulfuric acid was carried out on a very large scale in England, two factories alone, those at Queen's Ferry and at Gretna, producing 1300 tons per week. The lack of persons experienced in this industry and the extraordinary demand for the product caused many difficulties, which were overcome by close investigation of the processes. This record gives a description of the Gretna plant for the manufacture of nitric acid by the retort process, and its operation when running smoothly, together with reports of the investigations that greatly helped to this result. There are also sections devoted to the recovery of nitric acid from spent nitro-cotton acids by distillation, and the recovery of niter from the bags in which it was received, thereby diminishing the serious fire risk resident in niter-impregnated bags. It is interesting to note that while the niter content of these bags was greatly reduced by the combined processes of mechanical brushing and washing, the methods of operation were so developed as to show a considerable profit in the recovered niter, while reducing the fire risk.

As in previous publications in this series, the accounting is given in minute detail, presenting a pattern which other chemical manufacturers may easily follow. The data are visualized in numerous graphs and flow sheets, so that the course of a reaction, or the progress of a process and its behavior, may be viewed; and this is done, not only for current operations, but also for the results of investigations looking to improvements in operations or reductions in cost.

This, like the previous numbers, is a valuable contribution to chemical technology, but the style is so involved as to make the reading of the record unnecessarily difficult, while the fact that fundamental data, such as that of the "analyses" of niter on page 34, in which sodium nitrate is taken "by difference," foot up to less or more than 100 per cent, leads one to doubt if the printed data have been carefully checked.

Charles E. Munroe

The Chemistry and Technology of Gelatin and Glue.

By Robert Herman Bogue, M.S., Ph.D. McGraw-Hill Book Co., Inc., New York, 1922. Price, $6.00.

The extensive investigations and important results achieved in the last few years on these subjects or closely related ones have been bewildering in their erratic appearances in the various technical journals, and we welcome a summary of this work to which the author gives 268 pages. In connection with these references he discusses the theoretical aspects of the subject in a connected and clear manner. In some cases, when there is a difference of opinion among the investigators, he leaves the reader to arrive at his own conclusions.

Under the heading of "Structure of Gelatin," which is very justly given considerable space, is a discussion giving the troubles involved in the use of a revolving or oscillating disk or surface when studying the viscosity of gelatin solutions. In view of this one wonders why the MacMichael viscometer was chosen for the investigational work. However, as stated, all the viscometers available have their shortcomings when used for gelatin.

The second part deals with the technological aspects. The manufacture of hide and bone gelatin and glue, also casein, blood and fish glue, are described in detail.

The discussion on the tasting of glue and gelatins and especially the evaluation of these products, should be of interest to the user as well as the manufacturer.

There is ample evidence that the author has made very extensive and valuable investigations of this subject. However, on some points his results do not concur with other investigators—for example, as to the amount of pressure required on a glued joint, the "fallacy" of a starved joint, and relation of joint strength to grade.

The book is well printed on good paper with a few typographical errors, and should prove of interest not only to the manufacturer but also to the chemist who is confronted with the problem of specifying glue for his plant.

C. R. McKee

Yearbook of the American Pharmaceutical Association, 1920.

Vol. 9. lxxx + 865 pp. American Pharmaceutical Association, Chicago, 1922. Price, $4.00.

Notable among the features of the present volume of the yearbook is the larger number of abstracts of foreign pharmaceutical publications than has appeared in any of the previous editions since 1914. Under the general heading, "The Progress of Pharmacy," 692 pages are devoted to abstracts of the literature of pharmacy for 1920, classified under four general heads, Pharmacy, Materia Medica, Inorganic Chemistry, and Organic Chemistry, and 22 subheads. The whole has been carefully indexed to form an authoritative work of reference for the pharmacist. Eighty pages are devoted to the proceedings of the Association and the most recent revision of its constitution and by-laws, and 126 pages to lists of members both alphabetically and geographically arranged. It is to be regretted that circumstances have not permitted more prompt publication of this valuable book, but it is understood that efforts are under way to overcome this difficulty.

COMMERCE REPORTS

Notice—*Commerce Reports are received by all large libraries and may be consulted there, or single numbers can be secured by application to the Bureau of Foreign and Domestic Commerce, Department of Commerce, Washington, D. C. The regular subscription rate for these Commerce Reports mailed weekly is $3.00 per year (10 cents per single copy), payable in advance to the Superintendent of Documents, Government Printing Office, Washington, D. C.*

September

The **British dyestuffs licensing committee** plans to support the domestic industry by refusing import licenses when domestic dyes are available in adequate quantities and at reasonable prices. (P. 644)

A **new technical institute** is to be established at Salt River, a suburb of Cape Town, South Africa.

Statistics are given of the production of **minerals**, except coal and iron, mined in France during the first three months of 1922. (P. 661)

A successful flight has been made in Zealand, Denmark, by an airplane using **kerosene for fuel**. (P. 666)

A mixing plant has been erected at Hammersmith, England, for the production of a new **motor fuel** which is reported to give very good results. The fuel is said to be produced from a vegetable of Indian and Ceylon growth, and it is claimed that it can be sold much below current gasoline prices. (P. 666)

The Italian government has made appropriations for the exploration of **fuel deposits and oil**. It is hoped that within the next two or three years sufficient data will be collected to give an accurate idea of the value of the Italian subsoil with reference to its fuel contents. (P. 666)

Exports of chemicals and allied products from the United States to foreign countries for the seven months ended July 1922, were valued at $63,113,990, a drop of over $2,000,000 for the corresponding period in 1921. Decreases occurred in the exports of soda ash, pigments, paints and varnishes, fertilizers, and coal-tar products. Some of the chemicals showing increases were methanol, acetate of lime, calcium carbide, chloride of lime, copper sulfate, caustic soda, zinc oxide, ammonia sulfate, rosin, and spirits of turpentine. (Pp. 710–1)

The plants of the Alby Carbide Company and the Northwestern Cyanamide Company at Odda have been sold at auction. This marks the final collapse of two of the largest industrial undertakings in Western Norway and the practical bankruptcy of the community of Odda. (Pp. 711–2)

A plant for the **creosoting** of East African timber is being erected at Eldolat, 140 miles northwest of Nairobi. The plant will have a capacity of 500 tons per month. (P. 726)

The total production of the Baku, Grosny, and Ural-Emba **oil fields** for the first half of 1922 shows an increase of 17 per cent over the first half of 1922. (P. 730)

The discovery of an important deposit of **petroleum** near the Trans-Zambesia Railway is reported. (P. 730)

Reported **petroleum** fields in Sakhalin are said to be able to supply 10,000,000 tons of petroleum per annum. (P. 730)

It is believed by those who have visited Katanga Province that a source of **copper** production of world importance will be developed in the Belgian Kongo. (Pp. 777–8)

Recent prospecting near Vaux-en-Bugey (Ain) has revealed the presence of **methane gas** of sufficient importance and density to provide light for one-half of the city of Lyon. This is thought to be an indication that petroleum fields may be found in this vicinity and also at Abatilles (Gironde), where methane gas has also been found. (P. 787)

At present the utmost optimism prevails in **nitrate** circles and it is expected that sales during the next three months will be much larger than those already made. There are persistent rumors that large orders from Germany will soon be received, despite the difficulty of making payment. (P. 794)

Exports of iron ore from the mines in Lorraine during the first six months of 1922 show an encouraging increase over the export during the same period of 1921. Germany is taking an increasing proportion of this output. (P. 850)

Price is an important factor in successful competition in the importation of **artificial indigo** into China. When the selling price rises much above a certain point, the Chinese resort to greater use of natural indigo, which is produced in China and also imported from India. It is estimated that 60 per cent of the world's production of artificial indigo is consumed in China. (P. 795)

A copy of an unpublished report on the adoption of the **metric system** in Haiti may be obtained by applying to the Latin-American Division of the Bureau of Foreign and Domestic Commerce, or through the district and coöperative offices of the Bureau. (P. 817)

Statistics show the **copper** production of the Belgian Kongo for the first six months of 1922 to have been 19,842 metric tons, against a total of 13,030 tons for the corresponding period in 1921. (P. 850)

The production of **minerals** in Japan is declining. Statistics are given showing the production of minerals in June 1921, June 1922, and for the six months ending June 1921 and June 1922. (P. 851)

A report on the **vegetable-oil** products of Portuguese Africa, with statistics of exports from the principal ports in 1913 and 1920, is on file in the Foodstuffs Division of the Bureau of Foreign and Domestic Commerce, and may be examined by interested parties. (P. 854)

During the first week of July the new **Institute for Tanning Chemistry** in connection with the Technical High School at Darmstadt, Hessen, was formally opened. This school has for its object the further instruction of academic tanning chemists, as well as the promotion of scientific research in the field of tanning chemistry. (P. 857)

The following tabular statement shows the German output and domestic consumption of pure **potash** for 1913, 1921, and 1922.

	Output Tons	Consumption Tons
1913	1,110,362	557,000
1921	921,146	720,000
1922 (estimated)	1,250,000	850,000

There has been an increased use of **potash** in fertilizers for German soil because of the shortage of phosphoric acid. Only 268,000 tons of phosphoric acid were applied in 1921, as compared with 630,000 tons used in 1913. It is estimated that the former German potash mines in Alsace will yield 120,000 tons of potash in 1922, and that the Alsatian export capacity this year will be from 50,000 to 60,000 tons, while the German export capacity is estimated at 400,000 tons. (P. 859)

Interest in the utilization of the available water power at the Aswan Dam of the Nile River for the production of **nitrogen** for fertilizers has been revived, and the Egyptian government has published a bulletin entitled "The Fixation of Atmospheric Nitrogen," which may be consulted in the Chemical Division of the Bureau of Foreign and Domestic Commerce. (P. 859)

SPECIAL SUPPLEMENTS ISSUED

Australia
British South Africa
Czechoslovakia
France
Guatemala
Norway
Paraguay
Russian Foreign Trade
United Kingdom
U. S. Trade with Latin America in 1921

"Commerce and Finance in Czechoslovakia." ***Trade Information Bulletin* 53.**

"Conditions of Industries in Soviet Russia." *Trade Information Bulletin* **55.**

"French Trade in Petroleum Products." *Trade Information Bulletin* **54.**

STATISTICS OF EXPORTS TO THE UNITED STATES

GREECE—(P. 646)
Olive oil
SICILY—(P. 712)
Citrate of lime
SPAIN—(P. 776)
Olive oil
CANADA—(P. 864)
Pulp
Pulp wood

CURRENT PUBLICATIONS

NEW BOOKS

Agricultural Bacteriology. Joseph E. Greaves. Illustrated. Price, 21s. net. Constable & Co., Ltd., London.

Alcohol in Commerce and Industry. Charles Simmonds. 119 pp. Price, 3s. net. Sir Isaac Pitman & Sons, Ltd., London.

Analysis: Traité d'Analyse des Substances Minérales Métaux. Adolphe Carnot. Revised and enlarged with appendix by E. Goutal. 1050 pp. Price, 65 fr. Dunod, Paris.

Chemical Annual: Van Nostrand's Chemical Annual, 1922. John C. Olsen, Editor. 900 pp. Price, $4.00. D. Van Nostrand Co., New York.

Chemical Engineering Catalog. 7th annual edition, 1922. 1187 pp. Price, $10.00 (leasing privilege, $2.00). Chemical Catalog Co., Inc., New York.

Chemical Engineering: The General Principle of Chemical Engineering Design. Hugh Griffiths. 63 pp. Price, 3s. net. **Materials of Chemical Plant Construction. Non-metals.** Hugh Griffiths. 64 pp. Price, 3s. net. **The Weighing and Measuring of Chemical Substances.** H. L. Malan and A. S. Robinson. 63 pp. Price, 3s. net. **The Flow of Liquids in Pipes.** Norman Swindin. 64 pp. Price, 3s. net. **Chemical Works Pumping.** Norman Swindin. 80 pp. Price, 3s. net. Benn Brothers, Ltd., London

Chemistry: The Wonder Book of Chemistry. Jean Henri Casimir Fabre. Translated by Florence Constable Bicknell. 385 pp. Price, $2 50. The Century Co., New York.

Clay Products Cyclopedia. 252 pp. Price, $3.00. Industrial Publications, Inc., Chicago

Colloids: Fourth Report on Colloid Chemistry and Its General and Industrial Applications. Department of Scientific and Industrial Research. 382 pp. Price, 5s. 10d. H. M. Stationery Office, London.

Colloids: Die Methoden zur Herstellung Kolloider Lösungen Anorganischer Stoffe. The Svedberg. 3rd edition. 507 pp Price, 13s 2d. Th Steinkopff, Dresden and Leipzig.

Determination of Hydrogen Ions. W. Mansfield Clark. 2nd edition. 480 pp. Illustrated. Price, $5.00. Williams & Wilkins Co., Baltimore.

Dyes: The Manufacture of Dyes. John Cannell Cain 274 pp. Price, $4 50. The Macmillan Co., New York.

Glass: The British Glass Industry: Its Development and Outlook. W. E. S. Turner. 40 pp. Department of Glass Technology, The University, Sheffield, England.

Inorganic Chemistry. F. S Kipping and W. H. Perkin. 734 pp. Price, 8s. 6d. W. & R. Chambers, Ltd., London.

Oils: Examination of Hydrocarbon Oils and Saponifiable Fats and Waxes. D. Holde and Edward Mueller. 2nd edition. 572 pp. Price, $6.00. John Wiley & Sons, Inc., New York.

Organic Chemistry. W. H. Perkin and F. S. Kipping. 681 pp. Price, 8s. 6d. W. & R. Chambers, Ltd., London.

National Physical Laboratory. Collected Researches. 354 pp. Price, 20s. H. M. Stationery Office, London

Origin of Spectra. A. C. S. Monograph Series. Paul D. Foote and F. L. Mohler 250 pp. Price, $4.50. Chemical Catalog Co., Inc., New York

Paint: Physical and Chemical Examination of Paints, Varnishes, and Colors. Henry A. Gardner. 369 pp. Price, $9.00. Institute of Paint and Varnish Research, Washington, D. C.

Painters' Colours, Oils, and Varnishes. George H. Hurst. 530 pp. Illustrated. Price, $4.50. D. Van Nostrand Co., New York.

Patent Essentials for the Executive, Engineer, Lawyer, and Inventor: A Rudimentary and Practical Treatise on the Nature of Patents, the Mechanism of Their Procurement, Scientific Drafting of Patent Claims, Conduct of Cases and Special Proceedings, Including Forms. John F. Robb. 436 pp. Illustrated. Price, $5.00. Funk & Wagnalls, New York.

Patents for Inventions. J. Ewart Walker and R. Bruce Foster. 377 pp Price, 21s. Sir Isaac Pitman & Sons, London

Patents: Law Charts and Patent Engineering. H. H. Semmes and H. R Van Deventer. Price, $10.00. D. Van Nostrand Co. New York.

Petroleum and Allied Industries. J. Kewley. 302 pp. Industrial Chemistry Series, edited by S. Rideal. Price, 12s. 6d. Baillière, Tindall and Cox, London.

Problems of Modern Science. Arthur Dendy. 237 pp. Price, 10s. 6d. George G. Harrap & Co. Ltd., London

Progress and Science. Robert Shafer. 243 pp. Price, $2.50. Yale University Press, New Haven, Conn.

Rubber: The Reign of Rubber. William C. Geer. 344 pp. Price, $3.00. The Century Co., New York.

Tested Methods of Nonferrous Metallurgical Analysis. Seymour Pile and Reginald Johnston. 127 pp. Price, 7s. 6d. H. F & G. Witherby, London.

RECENT JOURNAL ARTICLES

Carburizing Materials: Tests of Carburizing Materials. O. A. Knight and T. C. Kern. *Forging and Heat Treating*, Vol. 8 (1922), No. 9, pp. 420–25.

Cement: Les Ciments à Haute Résistance. Jean Hendrickx. *Chimie et Industrie*, Vol. 8 (1922), No. 2, pp. 296–304.

Chemical Standards: Notes sur les Étalons Chimiques et sur leur Role dans l'Unification des Systèmes d'Analyse. Robert Adan. *Chimie et Industrie*, Vol. 8 (1922), No. 1, pp. 26–37.

Chemistry in the Service of the Community. Arnold Rowsby Tankard. *The Chemical Age (London)*, Vol. 7 (1922), No. 168, pp. 306–07.

Chrome Tanning: Le Tannage au Chrome à un Bain à Partir de l'Alun de Chrome. P. Chambard and L. Meunier. *Chimie et Industrie*, Vol. 8 (1922), No. 2, pp. 325–29.

Combustion of Gaseous Fuels Judged from Gas Analyses. A. G. Witting. *American Gas Journal*, Vol. 117 (1922), No. 12 (whole no. 3367), pp. 250–54, 256–61.

Dyes: Chemical Control of Dyestuffs. Walter M. Scott. *American Dyestuff Reporter*, Vol. 11 (1922), No. 7, pp. 225–28.

Dyes: The Practical Examination of Dyestuffs. Leon W. Sidebottom. *American Dyestuff Reporter*, Vol. 11 (1922), No. 7, pp. 248–52.

Electron Theory of Solids. J. J. Thomson. *Journal of the Franklin Institute*, Vol. 194 (1922), No. 3, pp. 281–89.

Fatigue of Metals: Recent Developments in Fatigue of Metals. H. F. Moore and T. M. Jasper. *The Iron Age*, Vol. 110 (1922), No. 13, pp. 779–84.

Ferric Salts as Solvents in the Leaching of Roasted Copper Ores. Percy R. Middleton. *Engineering and Mining Journal-Press*, Vol. 114 (1922), No. 11, pp. 451–54.

Gas Absorption and Oxidation Nonferrous Metals. B. Woyski and John W. Boeck. *Brass World*, Vol. 18 (1922), No. 9, pp. 266–69.

Glass: Modern Glass Factory Equipment. W. S. Mayers. *The Glass Industry*, Vol. 3 (1922), No. 10, pp. 197–99.

Graphites and Other Pencil Pigments. C. Ainsworth Mitchell. *The Analyst*, Vol. 47 (1922), No. 558, pp. 379–87.

Heat Balances of Blast Furnace and Steel Plants. W. Trinks. *Blast Furnace and Steel Plant*, Vol. 10 (1922), No. 9, pp. 451–56.

Iron: Experiments on the Ferrous-Calcium Chloride Solution for the Electrodeposition of Iron. W. E. Hughes. *Brass World*, Vol. 18 (1922), No. 9, pp. 261–65.

Leather: The Determination of Water-Soluble Matter in Vegetable Tanned Leathers. W J. Chater and D. Woodroffe. *Journal of the Society of Leather Trades' Chemists*, Vol. 6 (1922), No. 8, pp. 247–54.

Leather: Notes on Hide Soaking Experiments. B. S Levine. *Journal of the American Leather Chemists Association*, Vol. 17 (1922), No. 9, pp. 417–30.

Lubrication: The Technical Supervision of Plant Lubrication. I. Allen F. Brewer. *Industrial Management*, Vol. 64 (1922), No. 3, pp. 141–44.

Nitric Acid and Absorption Towers. J. A. Hall, A. Jaques, and M. S. Leslie. *Journal of the Society of Chemical Industry*, Vol. 41 (1922), No 16, pp. 285*t*–93*t*

Potash: La Question de la Cristallisation dans les Fabriques de Chlorure de Potassium. Ch. Rinckenbach. *Chimie et Industrie*, Vol. 8 (1922), No. 2, pp. 278–88.

Steel: The Trend of Specifications for Steel Castings. E. R. Young. *Blast Furnace and Steel Plant*, Vol. 10 (1922), No. 9, pp. 463–66.

Synthetic Resins: Les Résines Synthétiques. Clément and Rivière. *Chimie et Industrie*, Vol. 8 (1922), No. 1, pp. 38–40.

Tanning Materials: Comparative Observations of the Tanning Properties of Vegetable Tanning Materials, Synthetic Tans, and Mixtures of Vegetable Tanning Materials with Synthetic Tans. S. Kohn, J. Breedis, and E. Crede. *Journal of the American Leather Chemists Association*, Vol. 17 (1922), No. 9, pp. 450–60.

GOVERNMENT PUBLICATIONS

Notice—*Publications for which price is indicated can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C. Other publications can usually be supplied from the Bureau or Department from which they originate.*

Bureau of Mines

A New Instrument for Sampling Aerial Dust. LEONARD GREENBURG AND G. W SMITH. *Reports of Investigations* 2392. 3 pp. Issued September 1922.

Corrosion under Oil Films, with Special Reference to the Cause and Prevention of the After-Corrosion of Firearms. W. J. HUFF. *Technical Paper* 188. 26 pp. Paper, 5 cents.

Explosives Used in July 1922. W. W ADAMS. *Reports of Investigations* 2393. 5 pp. Issued September 1922.

Fatalities at Coal Mines in July 1922. W. W ADAMS. *Reports of Investigations* 2389. 3 pp. Issued August 1922.

Feldspar Mining and Milling. R. F. LADOO. *Reports of Investigations* 2396. 6 pp. Issued September 1922.

Gum-Forming Constituents in Gasoline. N. A. C. SMITH AND M. B. COOKE. *Reports of Investigations* 2394. 12 pp. Issued September 1922.

Ignition of Gas by Electric Detonators. L. C. ILSLEY AND A. B. HOOKER. *Reports of Investigations* 2383. 10 pp. Issued August 1922.

Production of Alumina Cream from Clay Tests on the Miguet Process. C. E. WILLIAMS AND C. E. SIMMS. *Reports of Investigations* 2393. Issued September 1922.

Tellurium. H. A. DOERNER. *Reports of Investigations* 2385. 3 pp. Issued August 1922.

Tests of Gas Masks and Respirators for Protection from Locomotive Smoke in Railroad Tunnels with Analyses of Tunnel Atmospheres. A. C. FIELDNER, S. H. KATZ, AND S. P. KINNEY. *Technical Paper* 292. 27 pp. Paper, 10 cents.

The New Albany Shale of Indiana. J. R. REEVES. *Reports of Investigations* 2390. 8 pp. Issued August 1922.

The White Clay Industry in the Vicinity of Langley, South Carolina. *Reports of Investigations* 2382. 6 pp. Issued August 1922.

Use of Geophone in Locating Compressed-Air Leaks. B. O. PICKARD. *Reports of Investigations* 2380. 2 pp. Issued August 1922.

Bureau of Standards

Standard Samples, General Information. *Circular* 25. Supersedes 6th edition issued June 20, 1917. 14 pp. Paper, 5 cents.

United States Government Specifications. Officially adopted by Federal Specifications Board, February 3, 1922, for use of departments and independent establishments of the Government in the purchase of materials covered by them.

- **Basic Sulfate, White Lead, Dry and Paste.** Standard Specification 6. *Circular* 85, 2nd ed. 9 pp. Paper, 5 cents.
- **Black Paint, Semipaste and Ready Mixed.** Standard Specification 14. *Circular* 94, 2nd ed. 8 pp. Paper, 5 cents.
- **Water-resisting Spar Varnish.** Standard Specification 18. *Circular* 103, 3rd ed. 6 pp. Paper, 5 cents.
- **White Paint and Tinted Paints Made on White Base, Semipaste, and Ready Mixed.** Standard Specification 10. *Circular* 89, 2nd ed. 10 pp. Paper, 5 cents.
- **Zinc Oxide, Dry and Paste.** Standard Specification 8. *Circular* 87, 2nd ed. 8 pp. Paper, 5 cents.

Bureau of the Census

Essential Oils. 14th Census of the United States: Manufactures, 1919. Prepared under the supervision of E. F. HARTLEY. 7 pp. 1922.

Explosives. 14th Census of the United States: Manufactures, 1919. Prepared under the supervision of E. F. HARTLEY. 8 pp. 1922

Fertilizers. 14th Census of the United States: Manufactures, 1919. Prepared under the supervision of E. F. HARTLEY. 12 pp. 1922.

Mines and Quarries 1919. 14th Census of the United States: Summary of the Census of Mines and Quarries for the United States. Prepared under the supervision of E. F. HARTLEY by F. J. KATZ. 47 pp. 1922.

The Rubber Industry. 14th Census of the United States: Manufactures, 1919. Prepared under the supervision of E. F. HARTLEY. 15 pp. 1922.

The Soap Industry. 14th Census of the United States, 1919. Prepared under the supervision of E. F. HARTLEY. 11 pp. 1922

Wood Distillation. 14th Census of the United States: Manufactures, 1919. 9 pp. 1922.

Congress

Investigation into the Prices and Conditions in the Oil Industry. Report submitted by MR. MCNARY from the Committee on Manufactures. *S. R.* 877. 8 pp. Ordered to be printed August 25, 1922.

Fordney-McCumber Tariff Bill of 1922. [illegible] Votes in the United States Senate on the bill and all amendments thereto. H. R. 7456 to provide revenue, to regulate commerce with foreign countries, to encourage the industries of the United States, and for other purposes. With Index. Compiled by C. A. [illegible]. *S. Doc.* 264. 118 pp. 1922.

Tariff Bill of 1922. Conference Report to accompany H. R. 7456. *H. R.* 1223. 162 pp. 1922.

Tariff Act of 1922 with Index. H. R. 7456—To provide revenue, to regulate commerce with foreign countries, to encourage the industries of the United States and for other purposes. *H. Doc.* 393. 198 pp. Ordered to be printed September 20, 1922.

Department of Agriculture

The Detection of Hypochlorites and Chloramines in Milk and Cream. PHILIP RUPP. *Dept. Bull.* 1114. 5 pp. Paper, 5 cents. Issued August 30, 1922.

Geological Survey

Antimony in 1921. F. C. SCHRADER. Separate from Mineral Resources of the United States, 1921, Part I. 8 pp. Published September 18, 1922.

Arsenic, Bismuth, Selenium, and Tellurium in 1921. V. C. HEIKES. Separate from Mineral Resources of the United States, 1921, Part I. 14 pp. Published October 5, 1922.

Asbestos in 1921. EDWARD SAMPSON. Separate from Mineral Resources of the United States, 1921, Part II. 8 pp. Published September 19, 1922.

Barytes and Barium Products in 1921. G. W. STOSE. Separate from Mineral Resources of the United States, 1921, Part II. 10 pp. Published September 11, 1922.

Clay in 1921. JEFFERSON MIDDLETOWN. Separate from Mineral Resources of the United States, 1921, Part II. 6 pp. Published September 20, 1922.

Feldspar in 1921. F. J. KATZ. Separate from Mineral Resources of the United States, 1921, Part II. 5 pp. Published August 30, 1922.

Gems and Precious Stones in 1921. B. H. STODDARD. Separate from Mineral Resources of the United States, 1921, Part II. 4 pp. Published September 13, 1922.

Mineral Resources of Alaska. Report of Progress on Investigations in 1920. A. H. BROOKS and others. *Bull.* 722. 266 pp.

Mineral Resources of the United States in 1921 (Preliminary Summary). Introduction by G. F. LOUGHLIN. Statistics assembled by M. B. CLARK from data furnished by specialists of the Division of Mineral Resources. 102 pp. Published September 14, 1922.

Nitrate Deposits in the Amargosa Region, Southeastern California. L. F. NOBLE, G. R. MANSFIELD, and others. *Bull.* 724. 99 pp.

Platinum and Allied Metals in 1921. J. M. HILL. Separate from Mineral Resources of the United States, 1921, Part I. 7 pp. Published September 19, 1922.

Primary Native-Silver Ores near Wickenburg, Arizona, and Their Bearing on the Genesis of the Silver Ores of Cobalt, Ontario. E. S. BASTIN. Separate from contributions to Economic Geology, 1922, Part I. 25 pp. Published August 2, 1922.

Salt, Bromine, and Calcium Chloride in 1921. K. W. COTTRELL. Separate from Mineral Resources of the United States, 1921, Part II. 7 pp. Published August 31, 1922.

Silver, Copper, Lead, and Zinc in the Central States in 1921. Mines Report. J. P. DUNLOP AND F. BEGEMAN. Separate from Mineral Resources of the United States, 1921, Part I. 31 pp. Published August 15, 1922.

Surface Water Supply of the United States 1917. Part XII. North Pacific Drainage Basins. B—Snake River Basin. Prepared in coöperation with the States of Idaho, Oregon, Nevada, and Washington. N. C. GROVER, G. C. BALDWIN, G. L. PARKER, AND F. F. HENSHAW. *Water-Supply Paper* 463. 168 pp. Paper, 15 cents.

Surface Water Supply of the United States, 1918. Part XII. North Pacific Slope Drainage Basins. C—Lower Columbia River Basin and Pacific Slope Drainage Basins in Oregon. Prepared in coöperation with the States of Oregon and Washington. N. C. GROVER, F. F. HENSHAW, AND G. L PARKER. *Water-Supply Paper* 454. 141 pp. Paper, 15 cents.

Surface Water Supply of the United States, 1918. Part VIII. Western Gulf of Mexico Basins. Prepared in coöperation with the State of Texas. N. C. GROVER, G. A. GRAY, AND C. E. ELLSWORTH. *Water-Supply Paper* 478. 106 pp. Paper, 10 cents.

Talc and Soapstone in 1921. EDWARD SAMPSON. Seperate from Mineral Resources of the United States, 1921, Part II. 7 pp. Published August 4, 1922.

Public Health Service

Notes on the Efficiency of Various Systems of Air-Conditioning in a Munition Factory. C. E. A. WINSLOW AND LEONARD GREENBURG. Reprint 729 from *Public Health Reports*. 17 pp. Paper, 5 cents.

MARKET REPORT—OCTOBER, 1922

[SUPPLIED BY DRUG & CHEMICAL MARKETS]

The broadest upward movement in prices noted at any time during the past two years sent American chemical values to higher levels during October. The passage of the tariff late in September was undoubtedly responsible for a goodly portion of the movement, although the effect of the new duties was felt coincidentally with the development of a number of scarcities in American markets. The two influences have been so intermixed that it is impossible to point out each product and the exact cause for its rise in price. The fact remains that numerous prices are higher, demand is better, and many chemical plants are beginning to resume operations.

As might have been expected prior to the passage of the Fordney-McCumber Tariff Act, numerous prices went up in anticipation of the higher rates which were considered certain to go through. Nevertheless, the actual passage of the bill was followed by a flood of further advances, particularly in the case of American-made products. At the higher prices, indications point to a resumption of operations by many manufacturers who naturally refused to produce at anything but minimum capacity while market quotations stood below cost.

Prices for heavy chemicals, including alums, bichromates, lead salts, prussiates, barium salts, Epsom salt, and others, are higher. Mineral acids, caustic soda, soda ash, and other products on which foreign competition has had little effect, were not materially changed. Oxalic acid has been an exception. Although the tariff was advanced from $1^1/_2$ cents a pound under the Underwood Law, to 4 cents in the Fordney Bill, October prices went down. Barium chloride with a duty of $25 per ton as against $5 formerly, naturally reacted sharply upward. Other barium compounds with higher duties also moved up. Epsom salt strengthened with a 50 cent per hundred duty as against 10 cents formerly. Potassium chlorate and sodium sulfide went higher. Cyanides remained free of duty after a sharp fight in Washington, and prices remained unchanged.

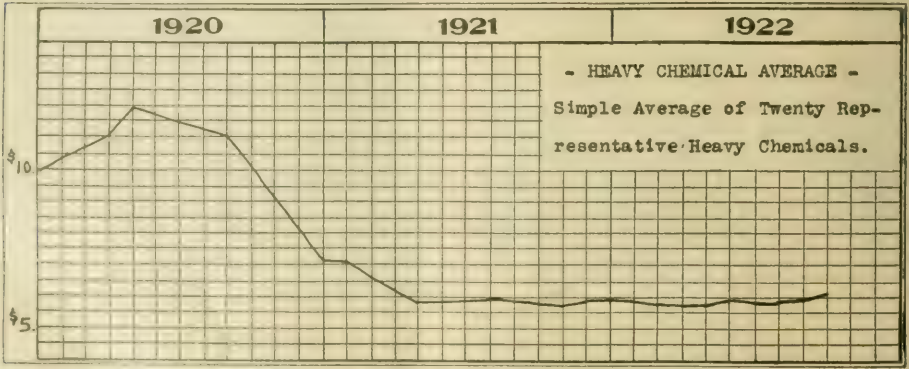
Among the items which have moved up in price independently of the tariff rates, might be included methanol, formaldehyde, hexamethylene, acetate of lime, acetone, arsenic, aniline oil, and aniline derivatives. Two sharp advances in methanol during October resulted from a depletion of available stocks and the elimination of two plants through failure. Owing to low prices, production has been practically at a standstill for many months. A freshened demand soon cleaned out most of the goods on hand and forced prices sharply upward. Formaldehyde has been advanced three times in as many weeks, owing to scarcity and the higher alcohol price. Hexamethylene is also up. Acetone is higher.

The scarcity of white arsenic has been acute and prices have continued to climb. In spite of the end of the consuming season in America, demand from manufacturers of arsenates has kept up. Supplies are far from adequate to take care of the demand. No duty was placed on this product in the new tariff. Aniline oil stocks have also been reduced to a minimum by a sudden springing up in demand. Little of this product has been produced for some time past, as a 12 cent and 13 cent market was under cost. Surplus stocks have been used up, and prices have jumped back up to 16 cents a lb. in large drums. Goods outside of producers' hands have been sold out. All aniline derivatives have also reacted to the higher price for the basic material.

Phenol staged further spectacular advances during October. In spite of the importation of close to 1500 drums from England on license prior to the passage of the new tariff, the goods went to consumers and open market figures rose. Nothing is to be had under 23 cents at 24 cents a lb. for big drums. With the Fordney tariff calling for 55 per cent and 7 cents a lb. on coal tars for other than medicinal purposes, cost to import phenol from abroad is said to be over 26 cents a lb. to-day. As far as is known, no American maker is producing now. All phenol derivatives have gone up, as might be expected. Three sharp advances in the salicylates were made during October, and with the present cost of phenol, current prices are stated to be still under cost of production. Technical salicylic acid is worth 32 cents and U. S. P. 35 cents a lb.

As far as medicinal and fine chemicals are concerned, sharp sweeping price advances during October were the order of the day. Within a month mercurial prices shot up about 25 per cent, owing to the rise in quicksilver costs. Manufacturers advanced mercurial prices three times. Bismuth metal and salts have also been moved up on two occasions. Caffeine is up. Tartaric acid, cream of tartar, and Rochelle salt are higher.

Manufacturers of synthetic and natural aromatic chemicals for perfume and flavoring purposes have been compelled to practically withdraw from the market as a result of the new tariff and the uncertainties which it has caused in the matter of aromatic prices. Until some definite price scale can be established on which tariff rates can be based accurately, importers' prices, which will have to be met by American producers, cannot be determined.



Courtesy of Drug & Chemical Markets

FIRST-HAND PRICES FOR GOODS IN ORIGINAL PACKAGES PREVAILING IN THE NEW YORK MARKET

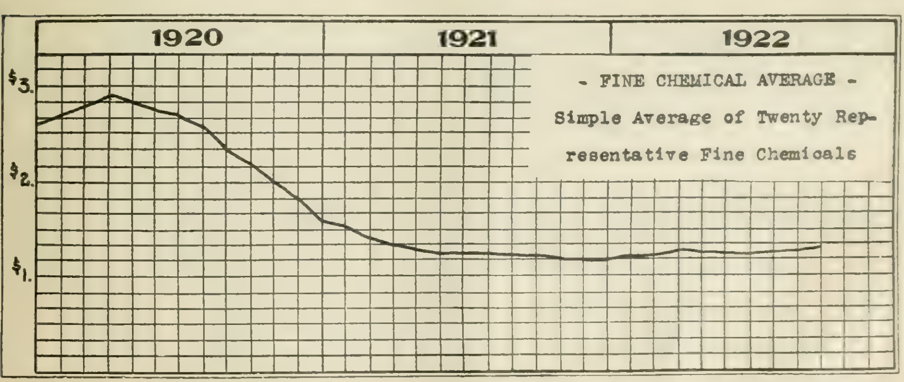
INORGANIC CHEMICALS

	Oct. 1	Oct. 15	Jun. 1922
Acid, Boric, cryst. bbls.......lb.	.11¾	.11¾	.12¾
Hydrochloric, comm'l. 20° lb.	.01¼	.01¼	.01¼
Hydrofluoric, 30% bbls..lb.	.07	.07	.07
Hydriodic, sp. gr. 1.150...lb.	2.25	2.25	2.00
Nitric, 42°, cbys. c/l wks.lb.	.06	.06	.06
Phosphoric, 50% tech.....lb.	.07½	.08	.10
Sulfuric, C. P............lb.	.08	.07	.07
66° tks. wks........ton	16.00	16.00	16.00
Oleum 20%.........ton	19.00	19.00	19.00
Alum, Ammonia, lump........lb.	.03½	.03½	.03½
Potash, lump............lb.	*.03	*.03½	*.03½
Chrome.............lb.	.06	.06	.07
Soda, ground............lb.	.03½	.04	.03½
Aluminium Sulfate (iron-free).lb.	.02½	.02½	.02½
Ammonium Carbonate, pwd...lb.	.10¾	.10¾	.08
Chloride, white gran......lb.	.07¾	.07¾	.07½
Ammonia, anhydrous ....lb.	.30	.30	.30
Ammonia Water, drums, 26°...lb.	.07½	.07½	.07½
Arsenic, white...............lb.	.09½	.10	.06½
Barium Chloride............ton	*105.00	*100.00	*53.00
Nitrate..................lb.	*.08	*.08	*.07
Barytes, white..............ton	33.50	33.50	28.00
Bleaching Powd., 35%, works ....100 lbs.	2.00	2.00	2.25
Borax, cryst., bbls............lb.	.05½	.05½	.05¾
Bromine, pure, wks...........lb.	.28	.29	.23
Calcium Chloride, fused, f.o.b. N. Y....................ton	24.50	24.50	28.75
Chlorine, liquid..............lb.	.06	.06	.06
Copper Sulfate..........100 lbs.	7.00	7.00	5.55
Iodine, resublimed...........lb.	4.40	4.40	3.80
Lead Acetate, white crystals...lb.	.11½	.11½	.11
Nitrate..................lb.	.22	.22	.15
Red......................lb.	.08	.09	.08
White (Carb.)............lb.	.07¼	.07¾	.07¼
Lime Acetate...........100 lbs.	2.75	3.00	1.75
Magnesium Carbonate, tech...lb.	.07½	.07½	.06
Magnesite calcined..........ton	55.00	55.00	55.00
Phosphorus, yellow...........lb.	*.25	*.25	*.27
Red.. ....lb.	*.26	*.26	*.30
Plaster of Paris.............bbl.	4.25	4.25	4.25
Potassium Bichromate........lb.	.09¾	.09¾	.10½
Bromide, imported.......lb.	*.16	*.19	*.13
Carbonate, calc., 80–85%.lb.	*.04¾	*.05½	*.04½
Chlorate, cryst...........lb.	*.07	*.07½	*.05½
Hydroxide, 88–92%......lb.	*.06	*.06½	*.06
Iodide, bulk.............lb.	3.50	3.50	2.90
Nitrate..................lb.	.08	.08	.08
Permanganate, U. S. P....lb.	*.15	*.17	*.15
Prussiate, red............lb.	*.90	*.90	*.29
Yellow..............lb.	*.37	*.38½	*.24½
Salt Cake, bulk.............ton	25.00	25.00	17.00
Silver Nitrate...............oz.	.47½	.47⅜	.44½
Soda Ash, 58%, bags.....100 lbs.	*1.80	*1.80	*1.85
Caustic, 76%, N. Y..100 lbs.	3.60	3.50	3.80
Sodium Acetate..............lb.	.07½	.07½	.04
Bicarbonate.........100 lbs.	2.00	2.00	2.00
Bichromate..............lb.	.07½	.07½	.07½
Bisulfite, powd...........lb.	.04¼	.04¼	.04¼
Chlorate.................lb.	.06¾	.06½	.07½
Cyanide, 96–98%........lb.	.23	.23	.28
Fluoride, tech...........lb.	.09½	.09½	.09½
Hyposulfite, bbls.....100 lbs.	3.20	3.20	3.50
Nitrate, 95%........100 lbs.	2.40	2.40	2.22½
Nitrite .... lb.	.09½	.10	.06½
Prussiate, yellow.........lb.	.24	.23½	.16½
Phosphate (di-sod.),tech..lb.	.04	.04½	.04¼
Silicate, 40°.............lb.	.01½	.01½	.01½
Sulfide, 60%, fused.......lb.	.04	.04	.05
Strontium Nitrate............lb.	*.10	*.10	*.10
Sulfur, flowers ....100 lbs.	3.00	3.00	2.75
Crude, mines.......long ton	14.00	14.00	16.00
Tin Bichloride, 50% sol'n......lb.	.10½	.10½	.09¾
Oxide. ....lb.	.38	.38	.37
Zinc Chloride, U. S. P.........lb.	.35	.35	.35
Oxide, bbls..............lb.	.07	.07	.08

ORGANIC CHEMICALS

	Oct. 1	Oct. 15	Jun. 1922
Acetanilide, U. S. P. bbls.......lb.	*.28	*.28	*.20
Acid, Acetic, 28 p. c.......100 lbs.	2.67½	2.67½	2.37½
Glacial..............lb.	.11	.11	.10
Benzoic, U. S. P........lb.	.55	.57	.60
Carbolic, cryst., U. S. P., drs...............lb.	.21	.24	.12
50- to 110-lb. tins....lb.	.28	.32	.18
Citric, crystals, kegs......lb.	*.50	*.50	*.43
Oxalic, cryst., bbls., wks..lb.	.17	.17	.14
Pyrogallic, resublimed....lb.	1.60	1.60	1.75
Salicylic, U. S. P.........lb.	.29	.35	.24
Tannic, U. S. P., bbls....lb.	.70	.70	.75
Tartaric, cryst., U. S. P...lb.	*.30	*.30	*.25
Acetone, drums ....lb.	.17½	.16½	.12
Alcohol, denatured, complete.gal.	.35	.35	.45
Ethyl, 190 proof, bbls....gal.	4.65	4.65	4.75
Amyl Acetate...............gal.	2.00	2.00	2.00
Camphor, Jap, refined, cases...lb.	.86	.86	.90
Carbon Bisulfide, c/l.........lb.	.06	.06	.06½
Tetrachloride............lb.	.10	.10	.10½
Chloroform, U. S. P., drums...lb.	.25	.25	.43
Creosote, U. S. P.............lb.	.40	.40	.40
Cresol, U. S. P...............lb.	.17	.17	.14
Dextrin, corn...........100 lbs.	3.09	3.09	2.70
Imported Potato.........lb.	.09	.09	.06½
Ether, U. S. P., 100 lbs.........lb.	.14	.14	.14
Formaldehyde, bbls...........lb.	.11½	.12¼	.10½
Glycerol, dynamite, drums....lb.	.16	.17½	.14½
Methanol, pure, bbls.........gal.	.80	.90	.75
Methylene Blue, med........lb.	3.00	3.00	4.00
Petrolatum, light amber......lb.	.04½	.04½	.05¼
Pyridine....................gal.	1.75	1.75	1.75
Starch, corn, pow'd......100 lbs.	2.47	2.47	2.13
Potato, Jap..............lb.	.07	.07	.06½
Sago.....................lb.	.03½	.03½	.04

*Resale or Imported (not an American makers' price).



Courtesy of Drug & Chemical Markets

OILS, WAXES, ETC.

	Oct. 1	Oct. 15	Jan. 1922
Beeswax, pure, white........ lb.	[illegible]	.32	.33
Castor Oil, No. 3.............lb.	.12	.13	.10½
Ceresin, yellow...............lb.	.08	08	.07½
Corn Oil, crude. tanks, mills...lb.	.07¼	07¼	.06¾
Cottonseed Oil, crude, f. o. b. mill.....................lb.	.07½	.07½	07
Linseed Oil, raw, c/l.........gal.	.88	.89	.69
Menhaden Oil, crude, mills...gal.	.38	.40	35
Neat's-foot Oil, 20°..........lb.	.20	18	16¾
Paraffin, 128–130 m. p., ref.....lb.	.03¾	.03¾	05
Rosin, "F" grade, 280 lbs....bbl.	6.55	6.75	5.30
Rosin Oil, first run..........gal.	.41	43	36
Shellac, T. N................lb.	.58	.56	66
Sperm Oil, bleached winter, 38°.....................gal.	1 30	1 17	1 70
Stearic Acid, double pressed...lb.	.09½	09¼	.09¾
Tallow Oil, acidless...........lb.	.10	.10¼	10
Turpentine, spirits of........gal.	1.33	1.43	82½

METALS

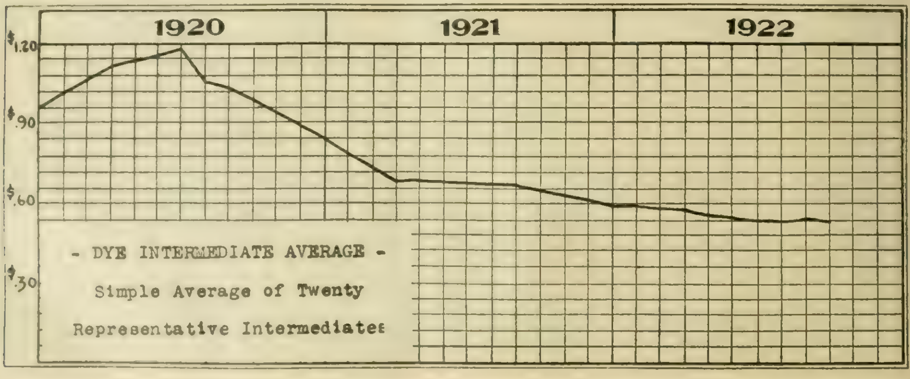
	Oct. 1	Oct. 15	Jan. 1922
Aluminium, No. 1, ingots.....lb.	.17½	17½	.17
Antimony, ordinary......100 lbs.	5.25	6.50	4.55
Bismuth.....................lb.	2.35	2.60	1.80
Copper, electrolytic..........lb.	.14	.14	.13⅞
Lake....................lb.	.14	.14	.13¾
Lead, N. Y.............100 lbs.	6.25	6.50	4.70
Nickel, electrolytic...........lb.	.39	.36	.45
Platinum. refined, soft........oz.	118.00	112.00	78.00
Quicksilver, flask......75 lbs. ea.	71.00	73.00	52.00
Silver, foreign...............oz.	.69	.69¼	.65¼
Tin.........................lb.	.32	.33	.32¾
Tungsten Wolframite....per unit	3.25	3.50	2.00
Zinc, N. Y..............100 lbs.	7.35	7.20	5.20

FERTILIZER MATERIALS

	Oct. 1	Oct. 15	Jan. 1922
Ammonium Sulfate, expt..100 lbs.	3.50	3.50	2.60
Blood, dried, f. o. b. N. Y....unit	4.00	4.00	3.50
Bone, 3 and 50, ground, raw..ton	28.00	28.00	30.00
Calcium Cyanamide, unit of ammonia	2.25	2.25	2.25
Fish Scrap, dried, wks......unit	3.80	3.80	3.25 & .10
Phosphate Rock, f. o. b. mine:			
Florida Pebble, 68%.....ton	3.00	3.00	5.00
Tennessee, 78–80%......ton	4.00	4.00	8.00
Potassium Muriate, 80%....unit	.60	.70	*.75
Tankage, high-grade, f. o. b. Chicago...............unit	4.00 & .10	3.85 & .10	3.00 & .10

COAL-TAR CHEMICALS

	Oct. 1	Oct. 15	Jan. 1922
Crudes			
Anthracene, 80–85%.........lb.	.75	.75	.75
Benzene, pure, tanks........gal.	.30	.30	.29
Naphthalene, flake...........lb.	.06½	.06½	.07½
Phenol, drums...............lb.	.23	.25	.11
Crudes (*concluded*)			
Toluene, pure, tanks.........gal.	.30	.30	.30
Xylene, 2 deg. dist. range, tanks..................gal.	.45	.45	.45
Intermediates			
Acids			
Anthranilic...............lb.	1.10	1.10	1.10
Benzoic, tech............lb.	.50	.50	.50
Cleve's..................lb.	1.50	1.50	1.50
Gamma...................lb.	1.80	1.75	2.25
H........................lb.	.75	75	1.00
Metanilic................lb.	1.00	1.00	1.60
Monosulfonic F..........lb.	2.30	2.30	2.30
Naphthionic, crude.......lb.	.60	.60	.65
Nevile & Winther's.......lb.	1.20	1.15	1.30
Picric...................lb.	.20	.20	.25
Sulfanilic................lb.	.17	.17	.26
Tobias'..................lb.	1.50	1.50	2.00
Aminoazobenzene............lb.	1.15	1.15	1.15
Aniline Oil..................lb.	.16	.16	.17
Aniline Salt.................lb.	.20	.24	.25
Anthraquinone (sublimed)....lb.	1.35	1.35	1.50
Benzaldehyde, tech...........lb.	.65	.55	.45
U. S. P..................lb.	1.40	1.40	1.25
Benzidine Base..............lb.	.85	.85	.90
Benzidine Sulfate............lb.	.70	.70	.70
Diaminophenol..............lb.	3.75	3.75	5.50
Dianisidine..................lb.	4.50	4.50	4.75
p-Dichlorobenzene...........lb.	.06	.06	.15
Diethylaniline...............lb.	.60	.60	.90
Dimethylaniline..............lb.	.32	.34	.40
Dinitrobenzene..............lb.	.20	.20	.21
Dinitrotoluene...............lb.	.20	.20	.25
Diphenylamine..............lb.	.52	.52	.58
G Salt......................lb.	.65	.65	.70
Hydroquinol.................lb.	1.15	1.15	1.35
Monochlorobenzene..........lb.	.08	.08	.10
Monoethylaniline............lb.	1.00	1.00	1.00
b-Naphthol, dist.............lb.	.22	.24	.30
a-Naphthylamine............lb.	.30	.30	.30
b-Naphthylamine............lb.	.95	.95	1.05
m-Nitroaniline...............lb.	.62	.62	.85
p-Nitroaniline...............lb.	.73	.73	.77
Nitrobenzene (Oil Mirbane)...lb.	.10	.10	.10
p-Nitrophenol...............lb.	.72	.72	.75
o-Nitrotoluene...............lb.	.09	.09	.15
p-Nitrotoluene...............lb.	.60	.60	.70
m-Phenylenediamine.........lb.	.90	.90	1.10
p-Phenylenediamine..........lb.	1.50	1.50	1.60
Phthalic Anhydride..........lb.	.35	.35	.38
R Salt......................lb.	.55	.55	.60
Resorcinol, tech..............lb.	1.30	1.30	1.50
U. S. P..................lb.	2.00	2.00	2.00
Schaeffer's Salt. ....lb.	.60	.60	.70
Sodium Naphthionate........lb.	.60	.60	.70
Thiocarbanilide..............lb.	.35	.35	.40
Tolidine (base)..............lb.	1.15	1.15	1.20
Toluidine, mixed.............lb.	.30	.30	.30
o-Toluidine..................lb.	.14	.14	.20
p-Toluidine..................lb.	.95	.95	1.10
m-Toluylenediamine..........lb.	.95	.95	1.10
Xylidine.....................lb.	.42	.42	.40



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EDITORIALS

Something for Nothing

IT REMAINED for our good friend, Arthur D. Little, to prove the incorrectness of the old adage that "you cannot make a silk purse from a sow's ear." It required a deal of patient research and persistent effort to accomplish the result. Our Government through the Civil Service Commission is now endeavoring to prove the incorrectness of another adage—namely, that "you cannot get something for nothing." But they propose to accomplish their result by the much simpler means of advertising and circularization by mail.

We refer to recent circulars announcing opportunities in government service involving some scientific training at salaries much lower than untrained men can command, and even less than unskilled labor is being paid in many parts of the country. It is proposed to offer $540 per year for a junior aid in one of the government bureaus. To qualify for this desirable place the applicant must stand a satisfactory examination in physics and chemistry, mechanical drawing, algebra, and geometry. He must also be able to say that he has fourteen units of high school training toward entrance requirements to a university, or that he has completed a high school course.

Another position pays $1000 per year. It is dignified by the title of Laboratory Assistant, and the applicant must stand examination in physics and chemistry, mathematics through trigonometry, and mechanical drawing, drawing to be made on the day of examination. Further, the applicant must show completion of sixty hours of college work with the grade obtained in each study pursued while in college.

These are typical requirements and salaries for a number of places for which applicants are desired. As the Commission points out, these are basic salaries, and if services prove satisfactory, a bonus of $20 per month is granted in addition.

By inquiring in your own locality you will have no difficulty in finding many untrained people with very much less investment of time and money in preparation, earning far better wages than the Government is offering not only the grades given as examples above, but men in very much more responsible positions. In announcing the resignation of the Director of the Bureau of Standards, a man under whose administration the Bureau of Standards has been developed from a very modest beginning to the most important bureau of its kind in the world to-day, the Secretary of Commerce again called attention to the extreme difficulty of satisfactorily carrying on the nonpolitical work of the Government on the scales of salary now set by law.

It seems to us that if government bureaus are to render the greatest service, they should, in general, undertake fundamental research upon problems so broad that the greatest number of people are benefited. Organizations capable of doing this work must include many of our best trained and experienced investigators. There are many such men now in government service, who, day by day, make a real sacrifice in order to discharge their duties. The Government must provide adequate salaries for scientific men. This whole matter is involved in the reclassification program that has long been discussed, and it is a matter of importance which must be kept before us.

The Committee on Public Representation of the Chicago Section has taken up the present situation with the Civil Service Commission. Its example might profitably be followed by similar committees in other Sections.

Adaptability

STATISTICS indicate a slow but consistent improvement in business affecting the chemical industry, by the number of people employed in the industry month by month, and the volume of export trade. The very welcome information comes to us that the outlook for chemists, both young and old, is much improved. Men have been taken on at some of the plant laboratories, and the consulting chemists are finding an increased demand for their services. With this return of better times and increased demand for chemists, let us do whatever we can to prevent a repetition of the sad experiences of many chemists in the past. We refer to the great turnover in the men employed in chemical laboratories.

We have frequently discussed the question of maintaining research organizations in times of business depression, and we still believe that research on a sufficient number of well-chosen problems should be consistently and continually carried on under proper direction as the best insurance for the future of any manufacturing organization. There are, however, many variables which may not be considered by those who unfortunately find themselves required to seek employment in new fields.

In many research organizations which have been more or less disrupted lately, the men constituting them were secured in a somewhat hurried manner during the period of war-time stress. There was an urgent demand for every man, and applicants who could show a college diploma and a little laboratory experience were accepted pretty much at their own valuation. They were available; they said they were qualified; and they were put to work. Most of these men did the best that could be done under the circumstances, but when the rush was over and business took a somewhat different turn, employers began to evaluate their men and naturally found there were some square pegs in round holes. There are too few real research men. Some men, try as they may, never become fitted for research although they may be very useful in other lines of scientific endeavor. We believe that a careful investigation would show the large majority of men who have proved themselves to be qualified for research still busily engaged. Nevertheless, employers who deliberately curtail research solely in order to show quick profits or to temporarily curtail expenditures are not to be excused.

We have been much interested in such work as Prof. C. E. Seashore, of the University of Iowa, is conducting to develop ways for discovering and encouraging students with exceptional ability. Perhaps our teachers can emphasize more strongly in the future than in the past the fact that the single word "chemist" is a definition altogether too broad to be applied to all those who work in that field. There is a modifying adjective that will make it apply far better in each individual case. Any help that can be given a chemist in selecting that adjective which really describes his qualifications will save a great deal of unpleasantness and in the end benefit the whole profession.

Standardization

THIS is not a new word. There are some folks who fear standardization in the belief that it means the loss of cherished individuality. The majority know that through standardization wonders can be accomplished in convenience, economy, and real service. Germany looks upon standardization as a means by which a firm hold can be gained in the great importing countries and possibly the whole world, if she can only impress her industrial standards upon world trade. On one order placed in Germany for Russian locomotives, twenty firms coöperated to such an extent that every part in every one of the seven hundred locomotives was exchangeable with a corresponding part in all the others. Obviously, the next order for locomotives will specify that all parts must be readily interchangeable with those on hand.

From its inception in 1917, the American Engineering Standards Committee has made satisfactory headway. More than one hundred sixty bodies of national importance coöperate in its work, and over five hundred individuals serve on its several sectional committees. Its objects are:

1—To unify methods of arriving at engineering standards, and to secure coöperation between various interested organizations, in order to prevent duplication of work and promulgation of conflicting standards.

2—To receive or pass upon recommendations for standards but not to initiate or develop the details of any particular standard.

3—To act as an authoritative channel of coöperation in international engineering standardization.

4—To promote in foreign countries the knowledge of recognized American standards.

5—To collect and classify data on standards and standardization bodies in the United States and foreign countries, and to act as a bureau of information regarding standardization.

Of the one hundred six projects before the Committee, eleven are concerned directly with chemistry and principally with standard methods of analysis and specifications. The American Society for Testing Materials has been the principal sponsor.

What can be done through standardization in an industry closely related to chemistry is illustrated by the experience of the Glass Containers' Association. Two hundred ten styles and sizes of prescription bottles have been reduced to twenty, and similar simplification seems possible in the list of bottles and jars now comprising four thousand separate items, exclusive of special names and trade marks.

The Standards Committee maintains a regular interchange of information in the form of quarterly reports as to the status of work under way with the national standardizing bodies of Austria, Belgium, Canada, Czechoslovakia, France, Germany, Great Britain, Holland, Italy, Japan, Norway, Sweden, and Switzerland.

Industries are coöperating with the American Engineering Standards Committee, and the Government, through the Division of Simplified Practice of the Department of Commerce, is actively assisting in the work of eliminating excessive variety and achieving other simplifications which decrease cost of production and distribution. Chemists and chemical manufacturers have a direct interest in this work. Costs must be reduced wherever possible. Standardization will be an important step in this direction.

November 9, 1922

DEAR MR. EDITOR:

In a few days my official connection with the Society will come to an end, and as I have been so happy in my relations with the entire membership, and so much genuine good and kindness have been showered upon me, I can't resist the impulse to send these lines of deep appreciation and gratitude with my

Goodbye!

EDGAR F. SMITH

The Chemist and His Work

THE University of Pittsburgh has selected fifteen contemporary chemists of the United States as seminar topics during the first semester. The graduate student to whom the assignment is made is expected to present a biographical sketch of the chemist assigned to him and to discuss the work of that chemist as represented by his three most important published papers. At the conclusion of the semester an examination will be held and credit given for satisfactory standing.

We believe seminars of this character are well worth while and that such a course of study will do much to give the chemist pride in his profession as well as worthy traditions to uphold. Our science is a living human thing in which interest can no doubt be increased by better acquaintance with the men and women identified with its development. The facts and theories associated with people are those best remembered. Mention of any of our greatest discoveries or inventions in any other field of endeavor immediately brings to the mind of the intelligent laity the name of the person credited with the work, and in nearly every other field manufacturers have not hesitated to advertise individuals until they are as well known as their creations. It should be so in chemistry, but chemists have not been so well advertised.

"Disarm or Perish"

LORD ROBERT CECIL sounded this warning in presenting the report of the Disarmament Committee to the Assembly of the League of Nations. In laying before the nations a choice between destruction and salvation, he stated that whatever agreements may be made—as at Washington—to limit the weapons of war, in a life and death struggle all weapons will be used.

In his discussion he mentioned the developments that have been continued as to size and effectiveness of aerial bombs, now said to be ten times as destructive as in the Great War, and laid stress upon the importance of poison gas and germs. It seems to be generally recognized, even by the League of Nations, that until the world really disarms those who would not be defenseless must give serious consideration to the purely scientific studies of poison gases and the methods of defense against them. In our country alone is the subject failing to receive that measure of support which means safety without aggression and without treaty violations. In the budget provided for another year, the item for our Chemical Warfare Service has been cut to the point where research is seriously threatened, if indeed is not made impossible. This is serious, not only from the standpoint of national defense, but because of the expert information which the Chemical Warfare Service is in position to supply on many questions of public welfare. We believe that the pendulum will eventually swing the other way, but it is very discouraging for those in that Service to endeavor to continue their work and maintain their trained organization under the present starvation policy.

Library Support

IT HAS been our experience that those in position to give financial support to scientific work are more easily interested in some investigation or research than in the publication of the results of such research. In many university departments one of the greatest difficulties is the maintenance of adequate library facilities, and doubtless much work is needlessly duplicated because records of the past are not accessible. Read again the letter on "Bibliography and Research," page 1085 of the November issue of THIS JOURNAL.

It is very encouraging to find that the Department of Chemistry of Ohio State University has just received a gift of $17,000, the income of which is to be used in developing the library of the department. In addition, the department will continue to receive its share of the university library funds. This is a type of endowment which should be sought, and we hope that the example that has been set by Mr. C. C. Sharp, the donor, may be speedily followed in many other universities and colleges. The Ohio State University is to be congratulated upon its good fortune.

Technical Exhibits

NO EFFORT to acquaint the scientist and industrialist with comparative progress in a given field of applied science quite takes the place of a national or international exhibition. To realize the most from the opportunities presented by such an exhibition, manufacturers will always display their best wares, models, or animated illustrations of them, and put their exhibits under the auspices of their leading specialists. Under such circumstances the ultimate consumer may gain valuable information from the men he meets, receive answers to his verbal questions, and make comparisons on the ground. Chemists realize what an impetus has been given to their industry by the National Exposition of Chemical Industries.

Now comes the initial effort in the closely related specialty —power. Under the guidance of an advisory committee whose personnel guarantees success, the First National Exposition of Power and Mechanical Engineering opens at the Grand Central Palace on December 7, and will continue through the 13th. The moving machinery which will be exhibited is sure to attract the crowd, but the important thing is to give the public a better understanding of what power means and the need for the conservation of the resources upon which power development depends.

This is of direct interest to every chemist, and particularly the industrial chemist, for he plays a vital part in power production, transmission, and utilization. The chemist is the one who has contributed most on the evaluation of fuels and the development of methods to control their utilization and insure efficient use. He has coöperated in devising materials for constructing power plants and transmission lines. The insulating problem has been a field for his knowledge and research. Bearing metals are not successfully produced without the chemist. Lubrication, so vital in all machine operations, is peculiarly the chemist's field, and offers him one of the most important groups of research problems, especially in view of our diminishing petroleum resources. In many other ways he has been directly concerned with that control over the forces of nature which we call power.

The power show will bring together the latest devices, the foremost experts, and a mass of instructive data, all of which offer a splendid opportunity which the chemist should not overlook.

Science in Trade

OF THE several movements under way for spreading a better knowledge of the application of chemical science to everyday affairs, none is more important than that recently initiated to teach chemical salesmen the rudiments of the science underlying their work. Chemists and educators are often inclined to slight the profession of the salesman and to consider him as one who has no particular interest in the science. Frequently an intelligent salesman is embarrassed to find that his customer knows more about his product than he does, especially where ordinary articles are being offered under fanciful names. No doubt the salesman has looked upon the chemist as an unnecessary evil, since frequently it has been the chemist who has been able to tell the salesman just what it is he has to offer. There has been a lack of understanding, neither chemist nor salesman realizing how intimately the work of one is related to that of the other.

In this new course being offered by F. E. Breithut at the College of the City of New York under the auspices of the New York Chapter of the Salesmen's Association of the American Chemical Industry, we have an interesting experiment. The salesman as the representative of the manufacturer carries a responsibility which he cannot hope to discharge fully without familiarity with the scientific viewpoint. It is true he cannot be given a chemical education through the medium of ten lectures, but from the enthusiastic reception of the plan by the salesmen, there is reason to hope that their interest may carry them beyond the initial course. But if not, the discourses upon the various phases of chemistry included in the course will be certain to stimulate interest and to create a better sympathy for the science and to make the salesman a much better representative of the chemical industry.

Why not go a step further and plan a course in chemistry for purchasing agents? This should not be confined to the purchasing agents of chemical plants, for to-day if any purchasing agent or buyer is really to know materials, he must have something of a scientific background. New products constantly coming on the market are mostly created with the aid of science and present a new problem to the totally unscientific man. To be sure, the day has gone when a certain purchasing agent refused to buy B. t. u.'s because he wanted heat, but there are many new specifications and novel materials and in order to pass upon them intelligently at least a speaking acquaintance with chemistry is essential.

When all the salesmen and purchasing agents become appreciative of chemistry, we shall have gone a long way toward gaining that intelligent sympathy of the public which is essential to our profession.

Section Programs

IN OUR November issue we offered to assist Local Sections in the interchange of information relative to their scientific programs. The first program which reaches us is in the form of a pocket card issued by the Rochester Section. On one side it gives a list of the officials of the AMERICAN CHEMICAL SOCIETY and of the Section, a blank in which the name of the member may be written, and a second line for the signature of the Secretary-Treasurer to denote good standing and dues paid. The other side of the card gives details of the meetings from the 30th of September to the 21st of May, with the names of speakers and their connection. In addition, special announcement cards are sent out before each meeting. Interest and good attendance are the rewards of such enterprise. Who has a better plan?

Heat Transfer by Conduction and Convection[1, 2]

II—Liquids Flowing through Pipes

By W. H. McAdams[3] and T. H. Frost[4]

Massachusetts Institute of Technology, Cambridge, Mass.

In this article a review of the literature has been made, including Reynolds' analogy between heat transfer and friction.

A simplified form of the theoretical Boussinesq equation is proposed for the film coefficient of heat transfer, h, for liquid flowing inside pipes in turbulent motion. This equation is based on dimensional considerations, and shows the relation between the coefficient, h, and thermal conductivity, diameter, linear velocity, viscosity, and density. According to this equation, the coefficient varies directly as approximately the 0.8 power of the product of linear velocity and density divided by the viscosity of the film, directly as the first power of the thermal conductivity, and inversely as approximately the 0.2 power of the inside diameter of the pipe.

This equation has been tested, with experimental data for water from four sources, and with data for light oils from two sources by plotting hD/k versus Duρ/z. As shown by Fig. 3, a straight line may be drawn through the experimental points on logarithmic paper. The coefficient may be predicted by use of Fig. 3, or from the equation of the curve:

$$h = \frac{22.6k}{D}\left(\frac{Du\rho}{z}\right)^{0.796} = \frac{22.6k}{D^{0.204}}\left(\frac{u\rho}{z}\right)^{0.796}$$

(For meaning of symbols, see Nomenclature Table.)

For water, since k = 0.329 and ρ is about 62, this equation becomes

$$h = \frac{199}{D^{0.204}}\left(\frac{u}{z}\right)^{0.796}$$

The fouling of pipes is discussed, and a factor of safety is suggested.

IN A PREVIOUS article[1,*] on this subject the authors pointed out the advantages of studying heat transfer from the point of view of *film* coefficients rather than *over-all* coefficients; this discussion is on the same basis.

Possibility of Two Types of Fluid Motion

It is well established that a fluid flowing through a pipe may assume either of two types of motion—namely, straight line (viscous) motion or turbulent (eddy) motion. A full discussion of this matter is given in a recent paper,[2] and it is there shown that the "critical" velocity—i. e., the average velocity of flow at which straight line motion tends to break over into the more common turbulent motion—is figured by the following equation:

$$u_c = \frac{16\mu}{\rho d f_c} = \frac{942\mu}{\rho} \qquad (1)$$

In this equation u_c is the critical velocity in ft. per sec.—namely, the cu. ft. per sec. flowing through the pipe divided by its cross sectional area in sq. ft.; μ represents the absolute viscosity of the fluid in lbs. per sec. per ft.; d represents the inside diameter of the pipe in feet, and ρ is the density of the liquid at its average temperature in lbs. per cu. ft. However, it was there shown that in some cases *unstable* viscous motion may develop, with the result that the break does not occur until the velocity becomes three times that calculated from the foregoing formula. In other words, the velocity at which one type of motion ceases and the other begins is rather uncertain. Nevertheless, calculations of critical velocity should be made in all cases, inasmuch as equations for the heat-transfer film coefficient for the common type of flow (turbulent motion) may not hold for viscous motion. This is because in turbulent motion the liquid at any cross section is continually being mixed by eddy currents, the main resistance being found in the relatively stationary film of liquid at the wall, whereas in viscous motion eddy currents are absent and the heat must flow between the pipe and the main body of liquid solely by the process of conduction through a layer which is thicker than in the case of turbulent motion. Fig. 1 shows how the critical velocity varies with the "kinematic" viscosity (μ/ρ) for a pipe 0.625 in. in diameter. $\left(\text{For other sizes multiply ordinates by } \frac{0.625}{\text{Act. D}}\right)$

Scope—The greater part of experimental data for the flow of liquids has been confined to the flow of water through pipes of various diameters. Fortunately, the velocities used in commercial practice are nearly always far above the critical velocity, and this paper will deal primarily with the flow of water under these conditions through tubes or pipes. The possibility of the two types of motion has been mentioned at this point for two reasons: first, because occasionally the cooling pipes through which the water flows may be so small and the velocity so low that turbulent flow will not be found; and second, because the flow of liquids more viscous than water will be touched upon in this article.

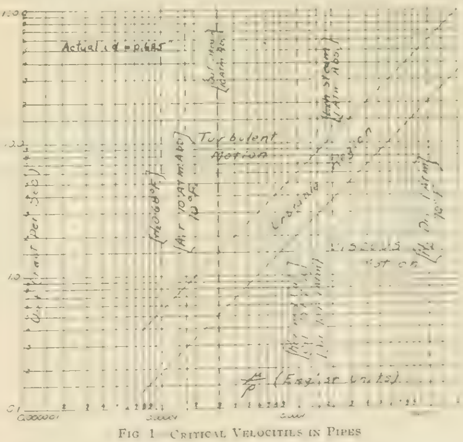

Fig 1—Critical Velocities in Pipes

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[1] Received August 21, 1922.

[2] Published as Contribution No. 77 from the Department of Chemical Engineering, Massachusetts Institute of Technology.

[3] Associate Professor of Chemical Engineering, Massachusetts Institute of Technology.

[4] Instructor of Chemical Engineering, Massachusetts Institute of Technology.

[*] Numbers in the text refer to the Bibliography, p. 1104.

THEORETICAL DISCUSSION

REYNOLDS' DERIVATION: ANALOGY BETWEEN HEAT TRANSFER AND FRICTION—In 1874 Reynolds[3] derived a *theoretical* equation for the coefficient of heat transfer for the case under discussion. This was based on the assumption of a certain relation between heat transfer and his law for the relation between the friction factor and a certain group of variables. The latter has been given a thorough test and found to be valid. His derivation is essentially as follows:

Consider a differential length, dx ft., of a pipe of inside radius r ft. through which water at the temperature t° F. is flowing at a rate of w lbs. per sec. and at an average velocity of u ft. per sec. The temperature of the inner wall of the pipe at this section is T° F., the specific heat of the water is C B. t. u. per lb. per° F., and the density is ρ lbs. per cu. ft.

1—By means of a heat balance, the rate of heat transfer per unit area of inner pipe wall ($Q/A\Theta$), expressed as B. t. u. per hr. per sq. ft., may be equated to the heat picked up by the water.

$$\frac{Q}{A\Theta} = \frac{3600\ w\ C\ dt}{2\ \pi\ r\ dx} \tag{2}$$

2—According to the familiar Fanning equation for friction, the loss of intensity of pressure is

$$dp = \frac{f\ dx\ \rho\ u^2}{gr} \tag{3}$$

where f is the experimentally determined friction factor and g equals the acceleration due to gravity, 32.2 ft. per sec. per sec.

3—Assume that the pressure lost due to friction ($\pi r^2 dp$) divided by the momentum of the water (wu/g) equals the heat transferred to the water divided by the heat which would have been transferred if the water had been warmed to the temperature of the wall.

$$\frac{\pi r^2 dp}{wu/g} = \frac{w\ C\ dt}{w\ C\ (T - t)} \tag{4}$$

By combining these equations one obtains

$$\frac{Q}{A\ \Theta\ (T-t)} = h = 1800\ C f \rho u \tag{5}$$

It should be noted that the last equation is Newton's law solved for the film coefficient of heat transfer, h, between the pipe wall and the water.

A careful inspection of Equation 3 shows that the friction factor has no dimensions. In 1883 Reynolds[4] predicted that f should be some function of certain variables grouped so as to have no dimensions. It was known that four variables affected f—namely, diameter, d, velocity, u, density, ρ, and absolute viscosity, μ. Noting that the dimensions of absolute viscosity in English absolute units are lbs. per sec. per ft., it is seen that the arrangement

$$\frac{du\rho}{\mu} = \frac{\text{(ft.) (ft./sec.) (lbs./cu. ft.)}}{\text{(lbs.)/(sec.)(ft.)}} \tag{6}$$

has no dimensions. Furthermore, it is the only one filling this requirement. Reynolds assumed the relation between f and $du\rho/\mu$ to be an exponential one, and this has been found from many experiments[4] to be the case. For *turbulent* motion f is found to vary as some exponent y, which changes very slowly with large variations in $du\rho/\mu$. The relation between f and $du\rho/\mu$ is shown in Fig. 2.

The right-hand branch of the curve is seen to be quite flat, although the slope is changing very slowly. For this branch, $f = a\ (du\rho/\mu)^y$, an average line would give

$$f = a(du\rho/\mu)^{-0.2} \tag{6a}$$

The left-hand branch, for viscous motion, has the equation

$$f = 16(du\rho/\mu)^{-1} \tag{6b}$$

the value of y being *constant.*

These predictions of Reynolds have greatly simplified calculations for the flow of liquids and gases through pipes, as values of f for all conditions may be read as ordinates from a single plot (such as Fig. 2) with $du\rho/\mu$ as abscissae. Practical application of this relation has been made elsewhere, but it was introduced here for reasons which appear below.

Instead of using f in Equation 5 as a variable, Reynolds substituted its equivalent from Equation 6*a*, obtaining for *turbulent motion:*

$$h = \frac{1800\ a\ C\ (\rho u^n)\ \mu^{1-n}}{d^{1-n}} \tag{7}$$

where, for convenience, $1 + y$ has been replaced by n.

This equation states that the film coefficient of heat transfer should be a direct function of the linear velocity, density and viscosity, and an inverse function of diameter. For example, for turbulent motion where $n = 0.8$ (and $y = -0.2$), this becomes

$$h = \frac{1800\ a C(\rho u)^{0.8}\mu^{0.2}}{d^{0.2}} \tag{7a}$$

In 1897 Stanton[5] tested this relation with his data for water flowing through 18-in. lengths of several small sizes (0.29, 0.42, and 0.55 in.) of copper tubes. The value of n for Equation 7 was found to be about 0.83, and Reynolds' equation allowed satisfactorily for variations in h due to velocity and diameter, *but did not allow for the actual effect of viscosity.* Stanton found empirically that Equation 7*a* divided by the first power of the viscosity would fit his data—namely,

$$h = \frac{a_1\ C\ (\rho\mu)^{0.83}}{d^{0.17}\ \mu^{0.83}} \tag{7b}$$

where a_1 is a new constant. However, Stanton abandoned Equation 7*b*, apparently because it was different from Reynolds' equation, and adopted the following *empirical* equation:

$$h = \frac{a_2(C)\ (\rho u)^{0.83}\mu^{0.17}\ (1 + \alpha T)(1 + \beta t)}{d^{0.17}} \tag{8}$$

where a_2, α, and β are new constants.

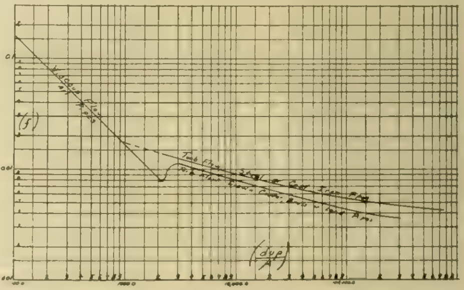

FIG. 2—VARIATION OF FRICTION FACTOR (f) IN EQUATION 3 WITH $\frac{du\rho}{\mu}$

DERIVATION OF RATIONAL FORMULAS—It seems strange that Reynolds did not apply the same process of "dimensional reasoning" to the heat transfer problem, which proved so valuable for the pressure drop relations. By definition, the film coefficient h equals the thermal conductivity k divided by the effective film thickness L—i. e., $h = K/L$. Values of k may be easily obtained from tables of physical constants,† so the only problem is the prediction of what variables determine L. L has linear dimensions. While both length and inside diameter fill this requirement, it does not seem reasonable that the length of the pipe has any effect on the coefficient. Since there are indications[6] that the zone of *relatively* low velocity in a pipe—referred to as the film of effective thickness, L—is directly proportional to the diameter of the pipe, other things being equal, it will be assumed that L varies as d. The effective thickness of film is known to be a function of several variables, such as velocity and viscosity. Since the friction factor and the

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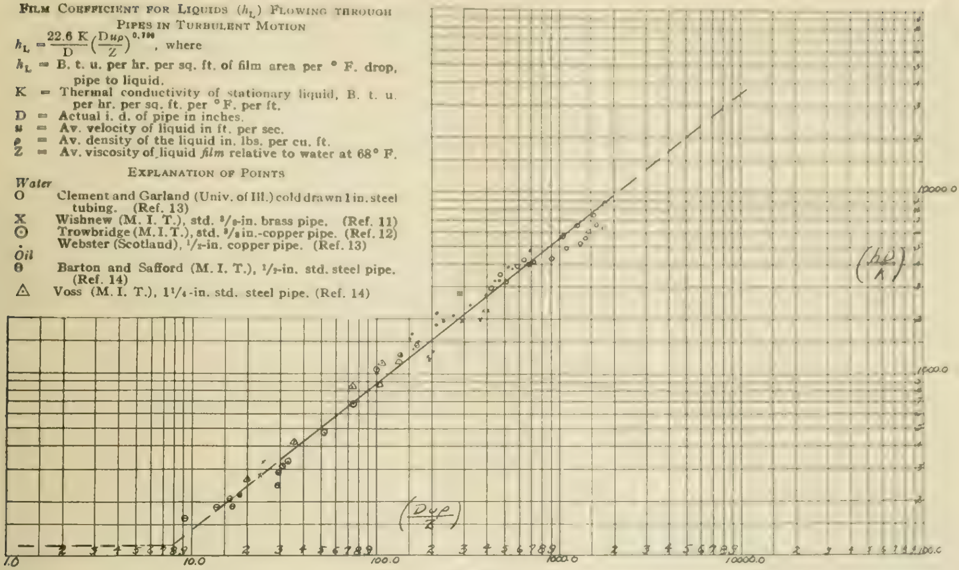
† See also Reference 1 for means of predicting k by H. F. Weber's equation.



FILM COEFFICIENT FOR LIQUIDS (h_L) FLOWING THROUGH PIPES IN TURBULENT MOTION

$h_L = \frac{22.6\ K}{D}\left(\frac{Du\rho}{Z}\right)^{0.786}$, where

h_L = B. t. u. per hr. per sq. ft. of film area per ° F. drop, pipe to liquid.
K = Thermal conductivity of stationary liquid, B. t. u. per hr. per sq. ft. per ° F. per ft.
D = Actual i. d. of pipe in inches.
u = Av. velocity of liquid in ft. per sec.
ρ = Av. density of the liquid in. lbs. per cu. ft.
Z = Av. viscosity of liquid *film* relative to water at 68° F.

EXPLANATION OF POINTS

Water
O Clement and Garland (Univ. of Ill.) cold drawn 1 in. steel tubing. (Ref. 13)
X Wishnew (M. I. T.), std. $^3/_8$-in. brass pipe. (Ref. 11)
⊙ Trowbridge (M. I. T.), std. $^3/_8$ in.-copper pipe. (Ref. 12)
• Webster (Scotland), $^1/_2$-in. copper pipe. (Ref. 13)

Oil
θ Barton and Safford (M. I. T.), $^1/_2$-in. std. steel pipe. (Ref. 14)
△ Voss (M. I. T.), $1^1/_4$-in. std. steel pipe. (Ref. 14)

1.0
10.0
100.0
1000.0
10000.0
100.0
1000.0
10000.0
$\left(\frac{D u \rho}{z}\right)$
$\left(\frac{hD}{k}\right)$

FIG. 3

film thickness are determined by the degree of turbulence $(du\rho/\mu)$, it seems reasonable to suppose that this same "dimensionless" ratio would determine the effective film thickness for heat transfer.

Hence, we assume

$$h = \frac{k}{L} = \frac{bk}{d}\left(\frac{du\rho}{\mu}\right)^n \tag{9}$$

where b and n are to be experimentally determined. It should be noted that this equation is a logical one, in that all dimensions cancel.

Rearranging,

$$h = \frac{bk\ (u\rho)^n}{d^{1-n}\ \mu^n} \tag{9a}$$

This checks with Stanton's experiments on viscosity. However, he apparently abandoned it and adopted Equation 8, which contains the two empirical correction factors for temperature. (In 1912, Stanton[7] derived Equation 9a for *gases* from Equation 7a by assuming that $C = a_3\gamma k/\mu$, neglecting variations in γ, the ratio of specific heat at constant pressure to that at constant volume, and assuming a_3 to be substantially constant.)

Equation 9a indicates that the film coefficent h for a given sized pipe and fluid varies directly as the product of the linear velocity and the density to the power n, and inversely as the viscosity to the same power. Furthermore, the slope of the curve or value of the exponent n theoretically may be predicted from the friction factor plot, since $1 + y = n$. Equation 9 indicates the general relation between the film coefficient h and linear velocity, density, viscosity, diameter, and thermal conductivity. It is obvious that the logical method of testing this theoretical relation is to plot hd/k versus $du\rho/\mu$ on logarithmic paper. If the theory is correct, the slope will be practically constant over a considerable range of $du\rho/\mu$, and b may be determined from the ordinate where $du\rho/\mu$ equals unity.

As a matter of convenience, diameter in *feet*, d, has been replaced by diameter in *inches*, D, and *absolute* viscosity in lbs./sec./ft., μ, has been replaced by *relative* viscosity in centipoises, z. Since water at 68° F. (20° C.) has a viscosity of 1.00 centipoise, the viscosity in centipoises is numerically the same as viscosity relative to water at 68° F., a concept which may be readily visualized. (It should be noted that z is the reciprocal of the relative fluidity f used in our preceding article.) Hence, we shall plot hD$/k$ versus D$u\rho/z$ to determine the value of b and n in the expression

$$h = \frac{bk}{D}\left(\frac{Du\rho}{z}\right)^n \tag{9b}$$

In 1909, Nusselt[8] applied the "principle of physical homogeneity" to the problem of predicting the relation between the film coefficient of heat transfer for *gases* and certain variables. As a result he obtained the following equation:

$$h = \frac{a_4k}{d}\left(\frac{du\rho}{\mu}\right)^n \left(\frac{C\mu}{k}\right)^m \tag{10}$$

He then *assumed* $n = m$, giving

$$h = \frac{a_4k}{d}\left(\frac{du\rho\,C}{k}\right)^n \tag{10a}$$

which is the same as the Boussinesq[9] equation derived in 1905. (However, Boussinesq did not test this theoretical equation with data in order to prove its validity and to determine the constants necessary for its use.) Nusselt used Equation 10a in correlating his data for various gases flowing inside pipes. This equation fitted the data very well, but mainly because of the use of the term $(u\rho)^n$. Other equations, employing $(u\rho)^n$, but containing terms different from those in Equation 10a, also fit the data.

It should be noted that Equation 9 may be obtained from the Boussinesq equation by placing $m = 0$. Instead of m being equal to n, or m being equal to zero, it may be that both m and n are finite, which would require a three-coordinate or "space" diagram instead of the one employed in Fig. 3. If this is true, the coördinates would be (hd/k), $(du\rho/\mu)$, and $(C\mu/k)$. It is possible that the Boussinesq equation may prove to be the ultimate general equation for the film coefficient of heat transfer for all fluids flowing in pipes.

In recent years Buckingham[10] has published papers dealing with dimensional equations for heat transfer for fluids flowing in pipes. While his equations were of the same general nature as those discussed above, they are not identical and apparently were not tested with experimental data.

EXPERIMENTAL DATA

WATER—Considerable data have been collected in these laboratories to determine the film coefficient of heat transfer for water flowing through pipes. The apparatus, which was similar to that described in our previous article, permitted the simultaneous determination of the coefficients, both on the water side and on the steam side. The coefficients were calculated from the data as previously described. In addition to these data collected by Wishnew[11] and Trowbridge[12] in connection with undergraduate theses, data for water from two other sources[13] have been calculated to our basis and are also shown in Fig. 3.

The range of variables in Fig. 3 is as follows:

	h	u	D	z	$Du\rho/z$
Lowest	150	0.6	$^3/_8$	0.3	25
Highest	2700	20.0	2	1.0	1800

OIL—On this same plot are included a few data for mineral oils of low viscosity. While these data[14] are not so reliable as those for water, owing to the lack of exact information concerning certain physical properties, yet they are compatible with them. Hence, in the lack of additional data for oil, the use of Fig. 3 is recommended for purposes of estimation.

Below the critical velocity $y = -1$, and since $y + 1 = n$, n should be equal to zero for viscous motion. Under these conditions Equation 9*b* reduces to

$$h = \frac{bk}{D} \qquad (9c)$$

No data are at present available to determine whether Equation 9c will hold under these conditions. Hence, the use of the plot below the critical velocity is not recommended. As shown by Equation 1, $du\rho/\mu = 16/f_c = 942$, at the theoretical critical velocity, which is equivalent to an abscissa in Fig. 3 of $Du\rho/z$ of about 7.6.‡ If unstable viscous motion develops, $Du\rho/z$ might be as high as 23. However, the probability of unstable viscous motion where heat is being transferred is remote. Hence, the curve in Fig. 3 should not be used below an abscissa of 8.

FOULING OF PIPES—It has long been known that in heat-transfer apparatus the inner surfaces of the pipes carrying certain liquids become covered with a deposit of solid matter. For example, where the cooling water contains dissolved bicarbonates such as calcium, these decompose under the action of heat and a scale of carbonate is formed. Further, a slime is often deposited, due to dirt in the cooling water. In the case of oils, deposits containing naphthalene, paraffin, and other materials may form. The scale or deposit in any case adds another resistance to heat transfer, which varies directly with the thickness and nature of the deposit. Allowance made for this should be by adding another resistance term to the denominator of Equation 1 of our previous article. Instead, it is customary to multiply the liquid film coefficient by a cleanliness factor, c_1, which never exceeds unity. The use of such a cleanliness factor is not theoretically sound, as in a given pipe containing a definite scale, the value of c_1 might be 0.4 with a very high liquid film coefficient and 0.8 with a very low coefficient.

In 1921, Frost and Manley[15] found the film coefficient in 2-in. standard steel pipe after two months' use with water decreased to 75 per cent of its value in the new pipe—i. e., $c_1 = 0.75$. After a thorough cleaning the original values were obtained.

When very bad cooling water is encountered, or where napthalene, paraffin, etc., may deposit from oils, a value of $c_1 = 0.5$ is suggested.

OPTIMUM VELOCITY OF LIQUID IN A CONDENSER

With data available for the film coefficient from condensing vapor to solid, it is possible to calculate the *over-all* coefficient in apparatus such as condensers, water heaters, etc., for any given conditions. Knowing the costs of heating surface and pumping,§ one can make an economic balance to determine the optimum liquid velocity. The method of calculation has been indicated in a recent paper[16] for the case of the heating of air by steam.

NOMENCLATURE TABLE

English Symbols

a (a_1, a_2, a_3) = Constants.
b = Constant
C = Specific heat of liquid = B. t. u. /lb./° F. = cal./g./°C.
d = Actual inside diameter of pipe in *feet*.
D = Actual inside diameter of pipe in *inches*.
f = Friction factor (no units).
g = Acceleration due to gravity = 32.2 ft./sec./sec.
q = Coefficient of heat transfer through liquid film inside of pipe = B. t. u./hr./sq. ft. of inner wall of pipe per ° F. difference in temperature between inner wall of pipe and liquid at the center line of pipe.
k(K) = Thermal conductivity of stationary liquid = B. t. u./hr./ sq. ft./ ° F. per foot of thickness.
L = Effective thickness of film, in feet.
m = Exponent.
n = Exponent = 1 + y.
p = Intensity of absolute pressure, lbs./sq. ft. of cross section.
Q = Quantity of heat transferred at right angles to heat transfer surface, B. t. u.
r = Inside radius of pipe in ft. = $d/2$.
T = Temperature of inner wall of pipe, ° F.
t = Temperature of water at center line of pipe, ° F.
u = Average water velocity, ft./sec.
w = Average rate of flow of water, lbs./sec.
x = Length of pipe in ft.
y = Exponent at average film temperature.
z = Viscosity of liquid at average film temperature relative to water at 68° F. (20° C.) as unity = centipoises.

Greek Symbols

α = Constant.
β = Constant.
γ = Ratio of specific heat of gas at constant pressure to that at constant volume.
π = 3.14.
ρ = Density of liquid at center line temperature, lbs./cu. ft.
μ = Absolute viscosity of liquid, lbs./sec./ft., = 0.0672 poises = 0.000672 centipoises.

BIBLIOGRAPHY

1—McAdams and Frost, *J. Ind. Eng. Chem.*, **14** (1922), 13.

2—Wilson, McAdams, and Selzer, *J. Ind. Eng. Chem.*, **14** (1922), 105.

3—Reynolds, *Proc. Manchester Lit. and Phil. Soc.*, **1874**, 8; see also Reference 4.

4—Reynolds, *Trans. Roy. Soc. London*, **1883**, 158. See also Stokes, *Math. and Phys. Papers*, **3** (1850), 17; Helmholtz, *Wissenschaftlichle Abhandlungen*, **1** (1873), 158; Rayleigh, *Phil. Mag.*, **48** (1889), 321; Lamb, "Hydrodynamics of Fluids," Cambridge University Press, 4th ed., p. 653.

5—Stanton, *Phil. Trans.*, **190A** (1897), 67.

6—Stanton, "The Mechanical Viscosity of Fluids," *Proc. Roy. Soc. London*, **85A** (1911), 366; "Collected Researches," National Physical Laboratory, **8** (1912), 73.

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‡ For smooth pipes f_c is about 88.3 per cent that in rough pipes, hence these values would be increased about 13 per cent.

§ Accurate data are now available for the calculation of the power required to pump fluids through pipes made of various materials. See Reference 2.

7—Stanton, "*Technical Report of Advisory Committee for Aeronautics*," **1912-13**, 45.

8—Nusselt, "Mitteilungen über Forschungsarbeiten," Heft **80-96** (1910).

9—Boussinesq, *Four. de Math. pur et appl.*, **1905**, 81.

10—Buckingham, *Phys. Rev.*, **4** (1914), 345; *Trans. A. S. M. E.*, **37** (1915), 263; *J. Wash. Acad. Sci.*, **4** (1921), 347.

11—A. Wishnew, Undergraduate Chem. Eng. Thesis, M. I. T., **1921**.

12—Trowbridge, Undergraduate Chem. Eng. Thesis, M. I. T., **1922**.

13—Clement and Garland, Univ. of Ill. Eng. Expt. Sta., *Bull.* **40** September 1909); Webster, *Trans. Inst. Eng. and Ship Builders in Scotland*, **57**, 58.

14—Voss, M. I. T., private communication; Barton and Safford, Undergraduate Chem. Eng. Thesis, M. I. T., **1921**.

15—Frost and Manley, Chem. Eng. Thesis, M. I. T., **1921**.

16—Lewis, McAdams, and Frost, *J. Am. Soc. Heating Ventilating Eng.*, **28** (1922), 97.

ACKNOWLEDGMENTS

Acknowledgment is made to Mr. A. Wishnew and Mr. L. W. Trowbridge of this laboratory for the use of their experimental data on water, and to Messrs. Voss, Barton, and Safford for their data on mineral oils. We also appreciate helpful suggestions made by Prof. Mayo D. Hersey in connection with the literature.

The Standardization of Laboratory Gas Cocks[1]

By S. W. Parr

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EVERY chemistry department is doubtless able to furnish a horrible example of the kind of gas cocks that should not be installed. Fig. 1 may serve as an illustration. The final appeal which seemed to carry weight in scrapping these cocks was the argument of a serious fire risk in a building already well supplied in that particular. Actual examples were not lacking by way of illustration.

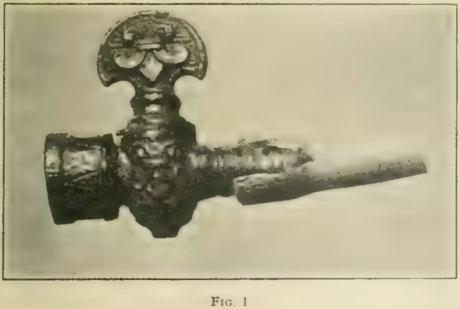

FIG. 1

The replacement of these old cocks by new ones of acceptable pattern, however, was found to be not a simple matter. One of the largest firms specializing in this sort of equipment recently filled an order in this laboratory for several hundred, of which Fig. 2 is an illustration. These were rejected as unsatisfactory, the reason being that rubber tubing, after serving for a time on cocks of the Fig. 1 pattern, or on burners of equally unfortunate dimensions as to hose connections, would form no attachment whatever for gas cocks like those of Fig. 2, and the fire risk would be again evident. The manufacturers argued that better tubing should be used; but the annual order in this laboratory is for an amount of burner tubing exceeding one mile in length, and an increase in cost for this item of 200 per cent seemed not to be appreciated by the manufacturer of brass goods.

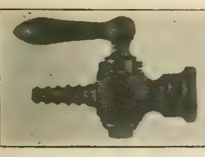

FIG. 2

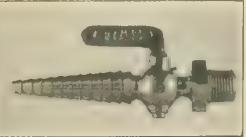

FIG. 3

Again, it was proposed recently to equip a number of new desks with the cock shown in Fig. 3. These were admitted only on the promise that they would be removed when a satisfactory substitute could be found. They are chiefly objectionable for the reason that a laboratory fully equipped with these cocks, including gas, air, and vacuum, is suggestive of the fretful porcupine. If the extravagant and useless waste of metal in the hose extension were put into an enlargement of the key and barrel, it would be an improvement. Fig. 4 presents a working sketch of a cock which one of the large factories has agreed to adopt to meet our own needs at least. With an order for approximately 500 cocks, it should be possible to obtain the exact pattern desired. The sketch is self-explanatory. The diameter of the smallest and largest corrugation in an extension length of $1^1/_4$ in. affords ample range for all reasonable variations of condition and size of rubber tubing. Attention may also be called to the fact that the outer edge of each corrugation has a slight angle and not a rounded surface. This operates with a sort of barb-like effect which permits of easy slipping on of the tubing and positive resistance to its removal. At the same time these angles are not so sharp as to produce cutting of the tubing.

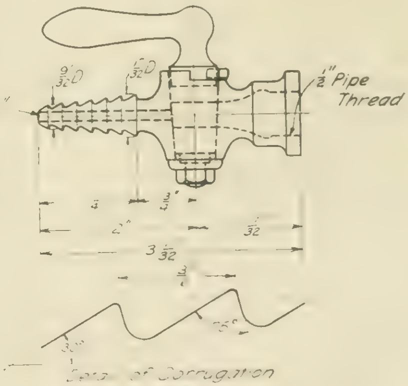

FIG. 4

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[1] Received September 20, 1922.

Some Recent Developments in the Manufacture of Natural Gas Gasoline[1]

By F. E. Hosmer and F. M. Seibert

Gulf Pipe Line Company, Houston, Texas

From the following discussion it is evident that wide choice of methods for recovering gasoline from casinghead gas is available. Most of the developments in recent years have been along the line of absorption. A comparison of the costs of installation and operation of the various methods, and a consideration of the yields of marketable product, indicate clearly (in the opinion of the writers) that absorption methods are the most practical. For those companies which have sufficient oil production and which run the oil to their own refineries, the best method to use is that of crude oil absorption. The plant construction is very simple and the shipping losses are considerably reduced, particularly so in case the oil is transported in pipe lines to the refiner.

THAT gasoline can be extracted from natural gas and casinghead gas has long been known, but its production has only within the past few years become of commercial importance, owing to the increase in the number of internal combustion engines.

In 1904 there were only two small plants producing casinghead gasoline. Both of these plants were somewhat crude, and their production for the year was only 400 barrels. At that time there was very little demand for gasoline, the products mostly desired being kerosene, lubricants, and fuel oil. In 1911 there were 176 plants in operation, and the production was 7,425,000 gal. In 1920 there were 650 plants, with a production of 483,000,000 gal. These figures portray the rapid growth of the industry.

CHEMISTRY OF NATURAL GAS

In the gasoline industry, natural gas is popularly classified in two great divisions—wet gas and dry gas. The gas coming from gas wells is generally classified as dry gas, and that coming from oil wells, if carrying any gasoline vapors, is considered as wet gas.

Natural gas is a mixture in which the hydrocarbons of the paraffin series predominate. Small proportions of nitrogen, carbon dioxide, and water vapor are usually present. In some cases natural gas contains as high as 35 per cent carbon dioxide. There is a record of one natural gas which contains 98 per cent carbon dioxide. A gas in which there is a large quantity of nitrogen may also contain helium. The recovery of this very light gas for use in the inflation of balloons is being attempted by the War and Navy Departments.

When a gas bubbles through or over a liquid, it takes up and carries along vapor or minute particles of the liquid. The proportion by weight of the vapor taken up increases as the temperature rises and as the pressure of the gas decreases, but is practically independent of the nature of the gas as long as no chemical reactions occur. When a natural gas comes in contact with petroleum in the earth, principally, those fractions of the petroleum having the lower boiling points are taken up, inasmuch as their vapor pressures are higher than those of the other fractions at the prevailing temperature. These vapors are carried with the gases in the same manner that water vapor is carried in air. Gases in oil-bearing formations thus mix with oil vapors, and the content of vapor in the gas in these formations is dependent upon the pressure and temperature, as well as upon the intimacy of contact between gas and oil. The effect of pressure is largely exerted through its influence upon the rate of diffusion of the vapor.

Obviously, gas from an oil well yielding a crude that contains no gasoline will not *pick up* any vapors. This condition exists in wells in the Gulf Coast District.

Other factors controlling the amount of vapor *picked up* by gas are as follows: the porosity of the oil-bearing strata, the depth of the well, and the rapid expansion of the gas which causes variations in temperature.

Inasmuch as the yield of gasoline from natural gas is largely dependent upon the proportion of the vapor of the liquid paraffins in the gas mixture, the character of the oil in a sand is of considerable importance. Crude oil is a mixture of several series of closely related complex hydrocarbons and of various other organic substances. There are often present several different compounds corresponding to a particular molecular weight, the boiling points of which lie so closely together that their separation by fractional distillation is impossible. The liquid hydrocarbons of chief concern to the gasoline industry are the pentanes, hexanes, and heptanes.

Natural gases in the oil fields of the United States are principally mixtures of methane, ethane, propane, butane, pentane, and hexane. Methane is always present in a stratum in the gaseous condition. Ethane becomes a liquid at 95° F. if the pressure reaches the value of 664 lbs./sq. in. Therefore, if a gas consisted of ethane alone and was subjected to a pressure in the earth of 664 lbs., it would probably be liquefied. In the case of a gas containing 50 per cent ethane and 50 per cent methane, a pressure of at least 2 × 664, or 1328 lbs., would be required to liquefy the ethane at 95° F. This fact is explained by discussion of the effect of partial pressures.

FRACTIONATION OF A TYPICAL WET GAS

	Per cent	
Methane	36.8	
Ethane	32.6	
Propane	21.1	
Butane-pentane	5.8	9.5
Hexane	3.7	

FRACTIONATION OF A TYPICAL DRY GAS

	Per cent
Methane	87.1
Ethane	5.0
Propane	6.5
Nitrogen	1.4

It will be seen that 9.5 per cent of this gas is liquefiable in plant practice. Based on 1000 cu. ft. of gas, the condensable portion will be 95 cu. ft. It takes about 32 cu. ft. of pure vapor of this character to make 1 gal. of gasoline. The 95 cu. ft. condensed would be about 3 gal. of liquid gasoline. The yield of such gas is usually expressed as about 3 gal. per 1000 cu. ft.

DESCRIPTION OF METHODS

The two most important methods of producing gasoline in the natural gasoline industry are the compression and the absorption processes. When using compression at pressures less than 100 lbs. the discharge from the compressors is passed through water-cooled coils into an accumulating tank where the condensate collects. The gas then passes out into the fuel lines, and gasoline is trapped off into stock tanks. Where high pressures are used, two-stage compressors are employed. Low-pressure cylinders compress the gas to about 50 lbs./sq. in., pass it through water-cooled coils and then through an accumulator where a portion of the vapor is condensed and trapped off to stock tanks. The gas passes out from the top of this accumulator and into the suction line of the high-pressure cylinders. It is then discharged through high-pressure water-cooled coils where additional condensate is obtained. In most cases the gas is next discharged into the fuel sytem. Compressing the gas to 250 lbs. pressure and cooling with water-cooled coils does not entirely strip it of its gasoline; therefore, further means of extraction are employed. One of them is to refrigerate the gas by means of an ammonia plant. Another way is to cool the gas by means of expansion in the following manner:

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[1] Presented before the Section of Petroleum Chemistry at the 63rd Meeting of the American Chemical Society, Birmingham, Ala., April 3 to 7, 1922

The gas, after leaving the water-cooled coils and accumulating tanks, passes through the inner pipe of a set of double pipe coils and into an accumulator. This takes place at 250 lbs. pressure. The gas then is used to drive an expander, which, in effect, amounts to using gas at 250 lbs. pressure to drive a prime mover, and this in turn compresses the exhaust gas from the power cylinders of the expander after it has been used as a cooling medium to compress the gas for distribution through the residue fuel system. By using high-pressure gas in this manner, heat is extracted from it in proportion to the work done, and the exhaust gas is consequently brought to a temperature in the neighborhood of −75° F. This exhaust gas, or expanded gas passing through the outer pipe of the double pipe coils, refrigerates the gas passing through the inner pipe. This causes it to drop out additional gasoline as it passes through the accumulator tank on its way to be used to drive the expander.

The temperature of the gas to be cooled may be lowered by this means to the neighborhood of 0° F.

Instead of using an expander, some plants use an absorber on the gas leaving the plant, in order to strip the remaining gasoline from the residue gas. The medium used as an absorbent is put through either steam or fire stills after it has scrubbed the gas, and the gasoline is driven off through condenser coils and blended with the regular plant product.

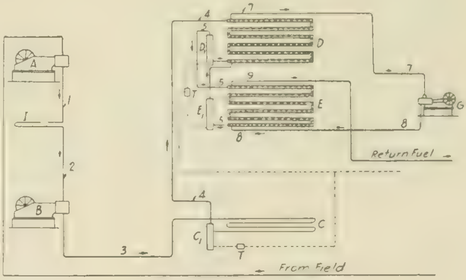
In order to understand changes that take place in a mixture of gases as it passes through the compressor, knowledge of the principles governing the pressures exerted by gas mixtures is essential, and it is necessary to become familiar with the general thermal relationships encountered.

One physical law must be explained—namely, that of partial pressures. We say that at sea level atmospheric pressure is about 15 lbs./sq. in. Three pounds of this pressure are due to oxygen in the air and 12 lbs. to nitrogen. When a vapor is mixed with other gases or other vapors and pressure applied, only a part of the total pressure is exerted on the first-named vapor, or, more correctly, is exerted *by* the first-named vapor. In case this vapor constitutes 10 per cent by volume of the mixture measured at total pressure, then the pressure on this vapor alone, or exerted by this vapor, is 10 per cent of the total pressure. A total pressure of 150 lbs. is required in order that a pressure of 15 lbs. be exerted on the first-named vapor and that condensation be made possible at the temperature of its boiling point. If we take noncondensable gas and add gasoline vapor to it to the extent that the mixture includes 10 per cent vapor and 90 per cent other gas, then, in order to place 15 lbs. pressure on this vapor, it would be necessary to place 150 lbs. pressure on the entire mixture; or, if the percentage were increased so that of the total mixture 20 per cent of this was condensable vapor, it would be necessary to apply only 75 lbs. pressure to obtain 15 lbs. pressure on the vapor. It must be understood that it is assumed that these vapors in question will be the first to condense, and that, of course, under these conditions condensation merely begins.

A LOW-PRESSURE METHOD

Under suitable conditions, gasoline vapor is condensed by removing its latent heat of condensation. In turn, gasoline will be evaporated by supplying the latent heat of evaporation. If by any means, therefore, we cause the evaporation of a given amount of gasoline, it must absorb heat from some source, and if we cause the evaporation of the gasoline to occur in heat-extracting relationship to a gasoline vapor (radiation losses being disregarded), the latent heat of condensation of the gasoline would be absorbed by that gasoline being evaporated. Approximately equal weights of gasoline and gasoline vapor must change state, the two processes occurring simultaneously.

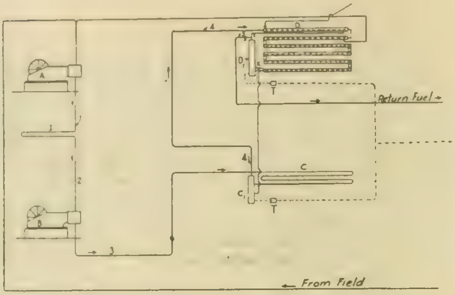
It has been shown that an increase of partial pressure will decrease the total pressure required to produce liquefaction at a given temperature. By evaporating gasoline for its cooling effect and by returning this gasoline vapor through vacuum pumps and compressor, it becomes intimately mixed with the gases entering from the field, thereby increasing the gasoline content of the gas to be handled by the plant. Such



Expander System

[1] This diagram shows the operation of the expander system A is a gathering pump from which gas, by means of line 1, passes through cooling coils I by means of line 2, to compressor B. From this, by line 3 through coils C into accumulator C_1, where any condensate that may be realized at 250 lbs. pressure is dropped out. Coils C will, of course, consist of high- and low-pressure coils, as at this pressure two stages will be used. From the accumulator tank C by means of line 4 the gas enters coils D, which are made up of smaller pipe on the inside of a larger pipe. Passing through coil D and into accumulator tank D_1, the ordinary procedure is for the gas to leave by means of line 5 and go direct to the expander G, which is nothing more or less than a means of using gas at 250 lbs. pressure as a means of power and to obtain the low exhaust temperatures accompanying its expansion. The exhaust gas leaves the expander cylinders by means of line 7, entering the other pipe of the double-pipe coils D, and after passing through this coil is allowed to escape into the fuel system, or, if the pressure makes it necessary, it goes into the compressor cylinders, driven by expander G, which are directly connected to the expander. Sometimes the gas, after passing through the double-pipe coils D, and out of the accumulator tank 5, will be very cold and used as a cooling medium before entering the expander. This means that its temperature will be higher when entering the expander and will be probably somewhat higher upon leaving the expander than it is in the case of the first-named arrangement. By this arrangement the gas, after leaving accumulator tank D_1 by means of line 5, enters the double pipe coils E, going into accumulator tank E_1, then through coils D, and by means of line 7 is led to the expander to be used as power, and the exhaust gas, by means of line 8, is used to cool gas going through coils E.

an increase in gasoline content provides that a greater percentage of the total pressure exerted on the gas is applied to the condensable part. It is then necessary that we extract from the gasoline vapors present in casinghead gas, only enough heat to reduce the kinetic energy to a value corresponding to that of the liquid state.



LOW-PRESSURE EVAPORATION

This diagram shows the arrangement used when the low-pressure evaporation system described in this paper is used. A represents a vacuum pump which gathers gas in the field. B is a single stage compressor. Gas passes from A through inner-cooled coils by means of line 1 and by means of line 2 enters compressor B, being discharged through line 3, is passed through coil C, into accumulator C_1, where any gasoline that may be condensed at this pressure and temperature is collected. By means of line 4 the gas enters double-pipe coil D, passing downward through this into accumulator tank D_1, where the remaining condensate is dropped out, owing to low temperature. This gas is dry and cold, and may be either discharged directly into the fuel lines or passed back through the top sets of coils to be used as a precooling agent and then delivered into the fuel lines. Gasoline from the accumulating tanks C_1 and D_1 is automatically trapped by means of trap T, off to stock tank. The amount of gasoline necessary for evaporation purposes, in order to refrigerate gas, is taken from accumulator tanks C_1 and D_1 at a point above the trap outlet, and is introduced at point marked X into the outer pipe of the double-pipe coils, or inner pipe, whichever the arrangement may be, where a slight vacuum is maintained, causing this gasoline to evaporate and absorb heat from the gas to be cooled. This evaporation is drawn off to point Y and drawn back to the vacuum pump where it is mixed with gas coming from the field.

There is no reason why we should arbitrarily assume that any particular pressure is necessary to condense gasoline from gas. We may take, for example, pentane, a constituent of casinghead gasoline. As a pure vapor, it would be necessary only to hold pressure on it which would equal its vapor tension at any given temperature. For instance, pentane has the following vapor pressures: 11.8 lbs./sq. in. at 86° F.; 8.1 lbs./sq. in. at 68° F.; 5.4 lbs. sq./in. at 50° F.; and 3.5 lbs./sq. in. at 32° F. Any one of these pressures suffices at the corresponding temperature.

The above-mentioned principles have been applied in several commercial plants, one of the writers having installed five of them.

It has been found in some instances that the boiling point of the liquid evaporated is as low as −60° F. The loss due to radiation through insulating material is overcome to a certain extent by precooling with cold dry gas expanded to field pressure, and it is assumed that the cooling realized by this cold dry gas is sufficient to offset the loss due to radiation in the evaporation coils proper. The amount of gasoline which it is necessary to evaporate is calculated, therefore, from the amount of gasoline recovered in the double-pipe coils. If a million cubic feet of gas which carries one-half gallon to the thousand are to be handled, and no water-cooled coils are used, it is then necessary to evaporate only slightly more than 500 gal. (0.5 of a gal. for each thousand cubic feet) of gasoline. The evaporation of the excess over 500 gal. provides for cooling the gas. This amount is very small, however, owing to the low specific heat of the gas.

The benefit of the principle of partial pressures and the advantages to be derived from increasing the partial pressure on the condensable part of the gas, are realized by the intimate mixture of the vaporized gasoline drawn from the evaporation coils with the gas coming from the field. This has the effect of increasing the amount of gasoline produced by the low-pressure coils, makes less work for the high-pressure cylinder of the compressor, at the same time effecting a greater amount of condensation even in the high-pressure coils. Results so far obtained indicate that the greater part of the gasoline evaporation in the double-pipe coils is recovered in the water-cooled coils, together with that part which would be recovered in the water-cooled coils if the evaporation coils were not in operation. If this were not the case the process would not be practical, since the gasoline recovered in the evaporation coils is due to evaporation of other gasoline, and this evaporated gasoline, if not recondensed before it reaches the evaporation coils, would make it necessary to evaporate twice as much, since there would be twice as much gasoline to recover. This gasoline would continually accumulate and in a very short time the apparatus would become inoperative. By increasing the percentage of condensable vapor in the gas, a greater percentage of the total pressure is exerted on the condensable part and, as explained before, because of this pressure more gasoline is condensed. The possibility of low temperature causing freezing of these coils was at first considered serious, but all inconvenience due to this source has been eliminated. One hundred and twenty-five pounds is the maximum pressure required under any circumstances in plant operation. In some instances, 70 lbs. has been found sufficient.

The question may be raised as to the horse power required to handle the additional amount of gas due to the evaporation of gasoline in the evaporation coils. As stated before, about 1 gal. of gasoline is evaporated in these coils for every gallon condensed, and in the case of a gas carrying 1 gal. per 1000 cu. ft. for a million feet there would be approximately 1000 gal. evaporated. This would amount to only 32,000 cu. ft. of gas for the entire million feet handled.

As to the actual horse-power requirements (based on the pressure of 125 lbs. which is used as a maximum), the following figures are presented in order to show the least possible difference we could expect to realize between the power necessary to operate this process compared with that necessary to operate under the high-pressure method.

Fifty horse power are required to compress 375,000 cu. ft. of gas per day of 24 hrs. from atmospheric pressure to 125 lbs./sq. in. 210,000 cu. ft. may be compressed to 250 lbs. pressure with the same amount of horse power. This figure is based on the practice of installing a 165-h. p. engine to drive a 660,000-cu. ft. compressor. However, we are giving this installation the benefit of an extra 40,000, assuming that it might handle 700,000 cu. ft. with this same 165-h. p. unit.

During a recent test at one plant, a meter-proving apparatus was installed which could be used at any time to serve the same purpose as a meter, and at different times the amount of gasoline being evaporated was checked. Since a gallon of gasoline will yield 32 cu. ft. of vapor, it was found that when the plant was handling 250,000 cu. ft. of gas per day, 22,000 cu. ft. of gas was the excess handled. These results would indicate that we could handle with 50 h. p., 345,000 cu. ft. of gas per day from the field. This test was made under average conditions—a temperature of 80° F. cooling in the water-cooled coils, and a very rich gas. The data show that 110,000 cu. ft. more gas can be handled per day than with a 50-h.p. unit at 250 lbs. pressure.

On the basis of one million cu. ft. for a vacuum station and gasoline plant under the same roof, the capacity would be as follows, the gas carrying $2^3/_4$ gal. per cu. ft. (vacuum taken at 18 in., which is the pressure generally used in designing a vacuum plant):

LOW-PRESSURE METHOD

1,000,000 cu. ft. from 18-in. vacuum to atmospheric pressure	77 h. p.	
88,000 cu. ft. from 18-in. vacuum to atmospheric which would be the excess due to evaporation	6.8 h. p.	
		83.8 h. p.
1,000,000 cu. ft. from atmospheric to 125 lbs.	127.4 h. p.	
88,000 cu. ft. from atmospheric to 125 lbs.	15.4 h. p.	
Total required to handle from 18-in. vacuum to 125 lbs. pressure and extract the gasoline		142.8 h. p.
		226.6 h. p.

HIGH-PRESSURE METHOD

1,000,000 cu. ft. from 18 in. to atmospheric	77 h. p.	
1,000,000 cu. ft. from atmosphere to 250 lbs. pressure	239 h. p.	
Total required from 18 in. to 250 lbs. pressure and extract the gasoline		316 h. p.

In addition, an expander would be required to secure maximum extraction with high-pressure method.

The amount of excess gas necessary to be handled is determined by the amount of gasoline left in the gas upon entering the evaporation coils, and no consideration is given here to the advantage derived from the removal of additional gasoline in the low-pressure side of a compressor, thereby causing the high-pressure side to do less work. It is quite probable that the greater part of the excess vapor is condensed in the low-pressure coils.

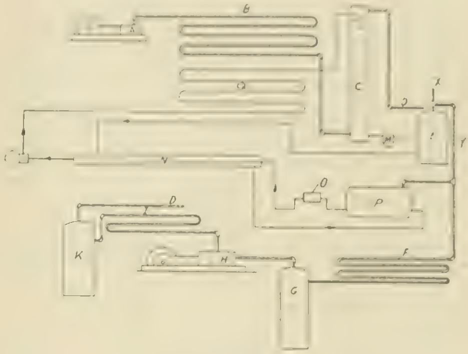
It was found at one of the gasoline plants, that when operating at 125 lbs. without the evaporation coils, 80° Bé. gasoline was made in the water-cooled coils. In a few minutes after placing the evaporation coils in operation, the gravity of the gasoline made in the water-cooled coils was 90° Bé., indicatting that considerably more gasoline is recovered in both the low- and high-pressure cylinders at 125 lbs. pressure in the water-cooled coils with evaporation coils in operation, than is recovered without them. This is due to the increased partial pressure of gasoline vapor corresponding to the increased content of gasoline, which makes possible the recovery of the additional gasoline.

It must be understood that the evaporation coils can be installed in connection with high-pressure as well as with low-pressure installations, and constitute a less expensive installation than an additional expander, besides having a greater heat-extracting capacity than the expander.

The advantages derived from the process herein described are: The installation cost is reduced in proportion to the horse-power requirements; with 125 lbs. maximum pressure the horse-power requirements indicate that a 40 per cent saving is to be realized in the initial expense, and a proportional saving in operating expense. In some instances where a lower pressure than 125 lbs. is adequate, there will, of course, be savings running up to as high as 60 per cent. The necessity of using an expander is eliminated, high pressure fittings and tanks are unnecessary, and an opportunity is offered to make installations of this process where the uncertainty as to the supply of gas would preclude the adoption of the high-pressure process. In most cases a plant of this type is assured of profits in a comparatively short time on account of the relatively low cost of installation.

ABSORPTION METHOD

This method consists in bringing the gas in contact with an absorbing medium in such a manner as to enable the absorbent to pick up the gasoline vapors. Plants of the usual type use an absorbing tower partially filled with absorbing medium, the gas being passed in at the bottom and out the top, while the absorbing medium passes in at the top and out the bottom. In addition, the absorbers are sometimes equipped with baffle plates, which assist in the further distribution of the gas and effect intimacy of contact between the absorbing medium and the gas.



ABSORPTION SYSTEM

This sketch shows diagrammatically the principles employed in absorption system. Gas is compressed by means of compressor A, passed through a set of water-cooled coils to the bottom of absorber C, out of the top of this absorber by means of line D, to be disposed of as dry gas. The absorbent oil is pumped by means of pump O, through a set of water-cooled coils, Q, into the top of the absorber, and is sprayed downward to point L. The oil leaves the bottom of the absorber, being trapped off automatically by M, into weathering tank E. From this weathering tank E the oil is passed through a heat exchanger where it comes in heat extraction relationship to oil leaving the stills. From this heat exchanger it goes direct to a still, P, where gasoline vapors are driven off through a set of water-cooled coils condensing these vapors and accumulating them in tank G. The oil leaves the still, passing through N on its way to pump O, and has been cooled somewhat by the oil leaving the weathering tank E on its way to the still. The oil, before going into the absorber, is further cooled by means of water-cooled coils Q. Vapors driven off in still P may not all condense in coils F; therefore, if this is of a sufficient amount, a compressor is installed which takes the vapors from accumulator tank G, which fail to condense in coils and discharge them through another set of water-cooled coils, I, where they are condensed and accumulated in tank K. If there happens to be any noncondensable vapors, these escape from the tank K into the air or fuel system by means of line D. Weathering tank E may be connected so that any vapors allowed to escape go into the atmosphere by means of line X or Y, being passed through water-cooled coils F, and in turn pass through condensing unit consisting of H, I, and K.

Absorption processes may be divided into two classes—those using solid absorbing materials that present large surfaces for contact, and those employing liquid absorbents. Activated charcoal and silica gel have been used in processes usually designated as absorbents of the first type. Crude oil, mineral seal oil, naphtha or low-grade gasoline may be used in processes of the second class. Everyone is familiar, of course, with the general character of these liquid absorbents.

The solid absorbents, however, need further discussion. During the war, chemists and physicists were called upon to develop an efficient gas mask. In their investigations charcoals were prepared which were found to be capable of absorbing condensable gases, because of the extensive surfaces within the body of the charcoal.

Investigations along these same lines have been carried out with silica gel. This gel is made by the coagulation of sodium silicate with an acid. The gel is washed and dried and is then ready for use. Certain very important precautions must be taken to prepare this material so that it will have sufficient surface to insure efficient absorption. In the use of either of these solids as an absorbent, two batteries of absorbers are required. The gas is passed through one battery until the material is saturated, when the gas is then diverted to the other battery. The saturated material is exposed to the action of superheated steam. The steam drives off the absorbed vapors that are carried with it to water-cooled coils, where both are condensed. The gasoline and water vapors are, of course, automatically disposed of. With plants using superheated steam, the necessity of drying out the material after distilling is eliminated.

It is claimed that these solid materials can be used as absorbents with considerably less expense than the ordinary method, owing to the fact that the heat losses of distillation are less. This claim, of course, reduces to a saving of fuel, and an investigation of the use of these solid materials can be limited to an investigation into the cost of fuel.

As the more popular method of absorption is the use of liquid absorbents, more detailed information is available than on the use of solids. The system is similar to that used for extracting benzene, toluene, and other vapors from gas made by destructive distillation. The gas under high or low pressures enters the absorbing towers placed in either vertical or horizontal positions and passes out the top. The oil used as an absorbent enters at the top, is sprayed downward, and leaves the absorbers at a point close to the bottom.

The absorbers usually consist of steel shells varying in diameter from 12 in. to 4 ft., although in some cases still larger diameters are used. The height varies from 15 to 45 ft. It is generally advisable to fill these absorbers partially with baffling material of some kind. In some cases there may be 6 ft. of baffling material and in others there may be 20 or 25 ft. Although the general plan has been to allow sufficient open space at the top of the absorbers for the separation of the oil and gas, one of the writers has recently installed absorbers 30 in. in diameter and 35 ft. high, filled to within 6 ft. of the top. A small separator for the outgoing gas, which removes any oil which may have been carried over, is superimposed. The baffling material varies—broken bottles, mineral-wool, broken stone, and bricks, etc., have been used. In some cases the baffling is made of wooden slats, and in still others flat revolving disks with small holes have been used successfully.

In the writers' opinion, the best baffles are steel plates. These may be about $^{1}/_{32}$ in. thick and from 6 in. to 12 in. high, and, of course, will be of varying lengths. The plates are bolted together with about $^{1}/_{2}$-in. space between. The lengths can be made to conform to the inner circumference of the shell. If sets of these baffles are placed one on the other, each set is at right angles to the one adjacent to it, or they may be placed so as to create a whirling motion, although such a motion does not present any advantage. The object of the baffling is to present a large surface for the oil to trickle over, thereby accomplishing intimate mingling of the gas and absorbent.

By using this steel baffling, arranged as described above, the area of the cross section of the absorbers is reduced by only approximately 3 per cent, thereby insuring a low velocity of the gas passed through the absorbers, without sacrificing contact surface.

The gas passing out of the top of the absorbers goes into the fuel system or into the air, depending upon the requirements. The oil after leaving the absorbers goes to stills, passing through heat exchangers in such a manner that it will be heated by hot oil leaving the stills, which in turn is cooled somewhat. The oil leaving the stills is then passed through water-cooled coils before being pumped into the absorbers.

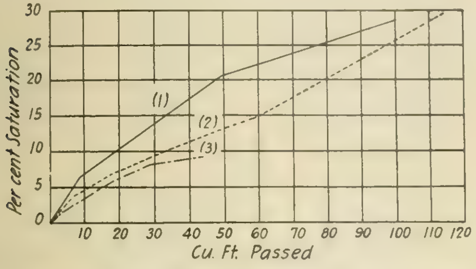
The apparatus for separating gasoline from the absorbent has been frequently described and will not be considered here.

The most important part of the absorption process is the action of the absorbers themselves. The amount of liquid absorbent necessary to be circulated depends upon the efficiency of the absorbers; this, in turn, depends upon the temperatures, pressures, and lengths of time of contact between oil and gas.

Henry's law states that the amount of vapor that will be absorbed by a liquid is proportional to the partial pressure of the vapor. This relationship is true, but the length of time of contact is of considerable importance in practice. For instance, the writers have noted in a plant operated at a certain pressure, and with gas of constant gasoline content, and using any given absorbent, etc., that if the length of time of contact alone was increased, the absorbent would dissolve increased quantities of vapor. This further absorption must be understood as not being of the same efficiency from the standpoint of stripping the gas of its content of vapor, as will be realized if low saturation percentages are maintained. We may assume, for example, that in an absorber in which the gas and oil are in contact for 15 sec. all the gas passing through will be entirely stripped of its gasoline. If this same oil is recirculated in the absorbers, however, and a further amount of gas brought into contact with it for an additional 15 sec., the oil will still absorb but the saturation percentage will not be doubled. By using the oil the second time, the saturation percentage will be approximately 80 per cent of that realized during the first period of absorption. If the operation is repeated, using this saturated oil and new gas, the oil will be further saturated, but will be increased only by about 50 per cent of that realized during the first period of contact. This latter ratio will prevail approximately, decreasing slightly until about 30 per cent total saturation is reached.

It has been customary in absorption plants to use saturation percentages varying from less than 1 per cent to about 6 per cent, depending upon pressures and temperatures. There is no reason, however, why this percentage could not be higher in practice. This would be accomplished primarily by increasing the length of time of contact, either by increasing the height of baffling or by operating absorbers in series. In doing this, the counterflow principle should be used. The rich oil leaving the absorbers meets rich gas entering and the lean gas leaving comes in contact with the lean oil entering. The effect of using this high saturation percentage would be to cut down the still capacity required, since there would be considerably less oil to be heated and the quantity of heat necessary to furnish the latent heat of evaporation would be the same. For example, if a plant with a capacity of 1,000,000 cu. ft. per day with a total gasoline content of 1000 gal. were running at a saturation of 4 per cent, 25,000 gal. of oil per day would have to be circulated through the absorbers, and the stills would have to supply sufficient heat to raise the 25,000 gal. of oil to the required temperature—in addition to latent heat of evaporation to be supplied for the 1000 gal. of gasoline. Now, if the saturation percentage were maintained at 20 per cent, it would be necessary to circulate only 7000 gal. of oil and to supply heat sufficient to raise the temperature of approximately 5000 gal. of absorbent to the temperature necessary to drive off the gasoline vapor, plus the latent heat of evaporation of 1000 gal. of gasoline. This would reduce the still capacity required, as well as that of the circulating pumps, by approximately 75 per cent. The same reduction would apply to the fuel requirements for the stills.

The writers have built commercial plants that employ these high baffles and absorbers in series, obtaining the high saturation percentages previously described. In actual plant practice, when handling in the neighborhood of 2,000,000 cu. ft. of gas per day at pressures between 20 and 30 lbs./sq. in. and saturation percentages up to 25 per cent, these baffles and absorbers have been found to be entirely satisfactory. It is noticeable that the increase in gravity is approximately one degree for each 5 per cent additional saturation. This applies also to crude oil when used as an absorbent. We have found in one particular case, with crude oil of 38° Bé. gravity and an initial boiling point of 118° F., that the crude oil, after being used as an absorbent, had a gravity of 43° Bé., and an initial boiling point of 80° F. This change in gravity represents an increase of approximately 25 per cent in volume, which was indeed the actual increase of volume observed. The temperature of the oil entering the absorbers was slightly less than 80° F., so that under this condition the temperature of the oil was about equal to the initial boiling point of the rich liquid, and the temperature of the oil leaving the absorbers was about 110° F. Since the oil leaving the absorbers was set at a temperature exceeding the boiling point of the absorbent at that place—i. e., original absorbent plus absorbed gasoline—its ability to dissolve further vapors was reduced. This effect was offset to some extent by increased pressures. The boiling points referred to above were determined at atmospheric pressure, and naturally, if the pressure were held at 20 or 30 lbs./sq. in., the initial boiling points would be somewhat higher. An absorbent will absorb vapor until the partial pressures of the dissolved gasoline constituents equal those of the same constituents in the wet natural gas at the common temperature.



COMPARISON OF MINERAL SEAL, CRUDE OIL, AND DRIP GASOLINE AS ABSORBENTS

Absorbents	Temperature—° F. Start	Temperature—° F. Finish	Gravity—° Bé. at 60° F. Start	Gravity—° Bé. at 60° F. Finish
(1) Mineral Seal	60	70	37.5	46.1
(2) Crude Oil	52	62	41.7	48.8
(3) Drip Gasoline	68	72	64.8	67.9

CRUDE OIL ABSORPTION

A means of reducing expense incident to recovering gasoline is the use of crude oil as an absorbent and pumping the rich liquid through pipe lines to a refinery. Some companies are at present blending the natural gasoline product with their crude oil runs.

Crude oil absorption is the same in principle, of course, as that obtained by the use of any other medium, the stripping stills in this case being eliminated, or rather replaced, by the regular crude stills of the refinery. It is necessary, in order that maximum efficiency be realized with a small amount of oil, to cool the oil after it leaves the absorbers. This requirement is due to the great amount of heat generated by the process of absorption. If the oil from the absorbers were put into tanks at these high temperatures, a considerable amount of the absorbed vapors would be driven off when the pressure is relieved.

An interesting feature in connection with crude oil absorption is the tendency for the oil to absorb dry gas in small amounts. However small in amount, such absorption is undesirable. A method for overcoming this objection is the use of the heat generated by absorption to maintain in the oil just before it leaves the absorbers temperature that will be high enough to offset this action at the pressures used. The oil coming in at the top trickling down over the baffles increases in temperature as its saturation is increased, and by the time it reaches the outlet it will be sufficiently high in temperature to prevent any trouble from this source.

It is interesting to note the comparative absorption values of mineral seal oil and crude oil. The accompanying chart shows this comparison. All the experiments were made with the same apparatus, using the gas from the same source, and under the same condition as to weather, etc.

A Chemical Family

Nine universities have contributed to the education of the chemical family of Swan, which sent a 100 per cent delegation—a father and three sons—to the Pittsburgh meeting of the AMERICAN CHEMICAL SOCIETY. These nine universities have already conferred upon this family ten degrees, including three Ph.D.'s, and the youngest son, Thomas, expects soon to qualify for his doctor's degree at Ohio State University.

The father, John N. Swan, is now head of the Department of Chemistry at the University of Mississippi. He has held professorships at three colleges, and has built a new laboratory at each.

Stewart D. Swan is connected with the Dentists' Supply Company of New York City, and William O. Swan is at present Acting Assistant Professor of Analytical Chemistry at the University of Virginia.

We wonder if this is not a record contribution to chemistry?

One of the important recent developments in the feldspar industry has been the rapid rise of New Hampshire as a feldspar-producing state. The unusual size and purity of the deposit now being worked near Keene, and the improved methods of mining and milling used have been responsible for this situation. The ore body stands nearly vertical between walls of mica schist. Between the feldspar body and the schist walls on each side occurs the mica for which the deposit was opened. The width of the pegmatite dike varies from 40 to about 200 ft. The total depth has not been proved, but mica workings to a depth of more than 200 ft. showed no apparent change in the nature of the deposit. Mica workings have also been extended over a length of 750 to 1000 ft. along the vein, with no change in the deposit indicated.

Refining of Gasoline and Kerosene by Hypochlorites[1]

By A. E. Dunstan and B. T. Brooks

THE ANGLO-PERSIAN OIL CO., LONDON, ENGLAND, AND THE MATHIESON ALKALI WORKS, INC., NEW YORK, N. Y.

Sulfur, though often present in relatively very small proportions, is the most objectionable impurity in motor fuel, and it is with the removal of sulfur that the present paper deals, although it should be pointed out that the refining method here described does a great deal more than merely remove sulfur. This method is not an academic process, but has been in successful large-scale operation or a little over one year and is now in operation in several refineries.

The advantages of the hypochlorite process for the refining of gasoline and kerosene, which are pointed out in this discussion, may be summarized as follows:

1—Lower refining cost.

2—Less loss on refining, adding materially to the total money saved.

3—No acid sludge is formed and no acid to be recovered.

4—The operation can be carried out in ordinary steel apparatus; one year's experience has shown that the corrosion of apparatus, piping, etc., is much less than when acid is employed. Lead-lined apparatus is not required.

5—The sum total of operation is easier to carry out than the acid-refining process with the acid recovery, etc., incident to the latter.

6—It is applicable to the light distillates from all types of crude petroleums.

IT WAS inevitable that with the tremendous growth of the petroleum industry and particularly the production of gasoline for motor cars, considerable attention would be given to better methods of refining. Considerable impetus has been given to this general problem by the automobile industry and, during the war, by the necessity of finding superior motor fuels and lubricants for aeroplanes. Petroleum refiners, or at least their sales departments, have also come to realize that superior goods are appreciated by the consumer.

The question of good motor fuel is certainly one of universal interest. This country, owning 85 per cent of all the automobiles in the world, produced 5,145,000,000 gal. of gasoline in 1920. At certain seasons the demand has been so great and the lapse of time from the production of gasoline at the refinery to its consumption has been so brief that refiners have often sacrificed everything to "through put." Shipments of gasoline from America to England, Australia, South Africa, and other points, have sometimes had to be returned to be re-refined, or have led to money settlements of no small magnitude. The export of gasoline to foreign countries requires that such gasoline be better refined than is the custom for domestic consumption. The utilization of high sulfur crude oils for gasoline production, the rapid increase in the production of "cracked" gasoline, the relatively insignificant production of very high-grade crudes, such as light Pennsylvania oil, the known merit of benzene in motor gasoline, and the very large losses resulting in the refining of crude benzene, have also been factors in the search for better refining methods.

Although the proper refining of gasoline involves more than the removal of sulfur compounds, the removal of such compounds can, nevertheless, be taken as a fair index of the degree of refining. The nature of the sulfur compounds present in a crude petroleum, or its distillates, makes a great deal of difference, for example, with respect to odor (mercaptans) and corrosive properties, but comparatively little is known as to their exact nature. Figures for the percentage of sulfur in unrefined gasoline distillates are not generally available, but average about one-tenth of the amount present in the original crude petroleum. The percentage of sulfur in a number of crude oils is given in the following table:

CRUDE	PER CENT SULFUR
Persia	1.0
California	0.55 to 3.55
Illinois	0.40 (average)
Louisiana (Jennings)	0.40 to 0.57
Indiana	0.72 to 1.26
Ohio (Lima)	0.65
Texas, Beaumont	0.94 to 2.40
Texas, San Antonio	1.52 to 2.02
Texas, Reeves County	1.00
Texas, Medina County	2.09
Texas, Travis County	1.26
Mexico	1.9 to 4.8

Engler and Höfer give the following sulfur contents of crude petroleum:

CRUDE	SULFUR PER CENT	CRUDE	SULFUR PER CENT
Tegernsee	0.044	Pechelbroun	0.650
Olheim	0.580	Wietze	0.58
Galicia	0.21	Roumania	0.170
Montechine	0.045	Bi-bilibat	0.220
Balachany	0.147	Palembang	0.212
Java	0.473	Sumatra	0.066
Roem Koot	1.166	Pennsylvania	0.049
Burmah	0.121		

Persian crude oil contains about 1.02 per cent and Burmah (Yenan Yung and Singu) about 0.1 per cent sulfur.

Free *hydrogen sulfide* has been identified in the crude petroleum from Canada, Ohio, Texas, Galicia, and Persia.[2] The natural gas accompanying sulfurous crudes sometimes contains upwards of 10 per cent of hydrogen sulfide. The hydrogen sulfide which frequently appears during distillation is probably partly expelled from solution and partly results from the decomposition of sulfur compounds in the oil.

Free Sulfur—Elemental sulfur has been recognized by Richardson and Wallace[3] in Texas petroleum, which, after being freed (at ordinary temperatures) from hydrogen sulfide and filtered through kaolin, deposited crystals of this element.

The natural gas accompanying petroleums rich in sulfur is usually rich in hydrogen sulfide, and the slow evolution of dissolved hydrogen sulfide from certain crudes has apparently been the cause of no small number of fatalities. Kraemer and Spilker[4] state that the presence of sulfur in petroleum is due to activity of certain bacteria, contemporaneous with the algae which these authors regard as the source of petroleum. It is well known that sulfur reacts readily with hydrocarbons to give hydrogen sulfide, and Friedmann[5] has shown that thiophenes are also formed. It is not difficult to conceive that such reactions have occurred in nature and would afford an explanation of the presence of sulfur derivatives in petroleum. However, a strong explanation against this explanation is the fact that thiophenes are rarely found in petroleum and then only in traces. Free sulfur is frequently observed in the neighborhood of petroleum wells, and it is not unlikely that this occurrence is due to reduction of sulfur compounds—e. g., mineral sulfates—by the oil or its antecedents. The observations of Steinkopf[6] that acetylene when passed over heated pyrites yields thiophene and that butadiene in a similar way generates methyl thiophene are of interest, though there is no satisfactory evidence of the occurrence of an appreciable quantity of acetylene, butadiene or thiophenes in crude petroleum. Speaking broadly, the thio compounds present in petroleum are distributed between all the fractions of the oil, but usually the larger proportion is found in the heavier distillates and particularly in the residues. Thus Perkin[7] describes an American crude containing 0.727 per cent sulfur:

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[1] Presented before the Section of Petroleum Chemistry at the 64th Meeting of the American Chemical Society, at Pittsburgh, Pa., September 4 to 8, 1922.

[2] Mabery, *Proc. Am. Acad. Arts Sci.*, **31** (1894), 1743; Thiele, *Chem.-Ztg.*, **25** (1901), 433.

[3] *J. Soc. Chem. Ind.*, **27** (1902), 316.

[4] *Ber.*, **35** (1902), 1212.

Fraction	Per cent Sulfur	Specific Gravity
to 90° C.	0.02	
110–150° C.	0.10	0.7282
152–220° C.	0.38	0.7669
220–257° C.	0.41	0.7940
257–300° C.	0.37	0.8138

Another oil from Petrolea, Canada, containing 0.98 to 1.06 per cent sulfur gave the following results:

Fraction	Per cent Sulfur	Fraction	Per cent Sulfur
115–150° C.	0.28	250–300° C.	0.51
150–200° C.	0.42	300–350° C.	0.86
200–250° C.	0.50	Residue	0.70

ELIMINATION OF SULFUR FROM PETROLEUM DISTILLATES

It has long been established that sulfur compounds occurring in petroleum products are objectionable, and are largely responsible for the properties which refining seeks to remove. While this statement applies to nearly all[8] petroleum products, it is particularly true of gasoline and kerosene. The offensive odors possessed by most unrefined gasolines are due chiefly to very small proportions of mercaptans, and perhaps to a lesser extent to nitrogen bases and simple naphthenic acids. Unrefined gasolines are also usually corrosive to metal, copper being usually employed for the test, and this also is attributed to sulfur derivatives or perhaps to dissolved elementary sulfur. Gasolines and kerosene of offensive odor also usually show a positive "Doctor" test (with alkaline litharge solution). In addition to the effects of sulfur just mentioned, the use of high sulfur gasolines, particularly benzene blends which are apt to have a high percentage of sulfur, results in the formation of acids on combustion in a motor, and this causes serious corrosion. The discoloration and development of acidity in gasoline that is stored for some time is also frequently attributed to sulfur compounds, although these effects are certainly more pronounced in the case of cracked oils which have been refined by sulfuric acid, as pointed out below. Sulfur is probably not such a serious impurity in kerosene as in gasoline, although it is known to cause filming of lamp chimneys and charring and uneven burning of the wick. It is also probably responsible for discoloration during storage.

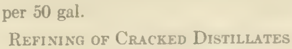
The best known and one of the most successful processes for desulfurizing oils is the Frasch process, developed to sweeten the so-called "skunk" oils of northern Ohio, Indiana, and Ontario. The production of this crude has now sunk to very insignificant proportions, and other oils which are now of the greatest industrial importance—for example, the high sulfur Mexican oils—cannot be successfully desulfurized by the Frasch method. Frasch also took out a patent[9] for *dechlorinating* oil which had been treated with bleaching powder. The Frasch method of dechlorinating consisted in heating the oil with alkaline litharge or Doctor solution, but so far as the authors are informed this process was never operated on an extensive scale. Colin and Amend[10] patented a method of refining petroleum distillates which consisted in treating the oil with hypochlorites in the presence of catalytic agents, such as manganese, nickel, or cobalt salts, which evolve oxygen from the hypochlorite. However, the only desulfurizing process other than that of Frasch which has been employed on a large scale is the alkaline litharge method; but, like the Frasch method, this process eliminates only certain classes of sulfur derivatives and is of little or no value on distillates from certain crudes. It is frequently noted that gasolines may be negative to the alkaline litharge test and yet show very marked corrosion of copper and rapid discoloration on standing.

The method of refining by dilute hypochloric solutions described below seems to be universally *applicable to desulfurizing all the gasoline and kerosene distillates from all types of crudes.* For example, it can be successfully applied to the desulfurizing and refining of naphtha from Mexican crudes, which are not amenable at all to the Frasch method. It should be pointed out also that under the conditions as defined below no chlorine is introduced into the oil. Refining by hypochlorite can be carried out according to either of two principles: (1) complete desulfurization, or (2) refining so as to pass the usual tests and be satisfactory as regards odor, color, and keeping qualities. The latter method requires the employment of much less reagent and is accordingly cheaper. Although the copper corrosion and Doctor tests may be negative and the oil may be quite satisfactory in other respects, not all the sulfur present is actually removed; the corrosive and offensive sulfur compounds present are converted to very stable compounds which are odorless and noncorrosive. The amount of hypochlorite required to refine the gasoline distillate from the average American crude petroleum is remarkably small.

The savings effected by the hypochlorite method vary widely with different oils and according to the degree to which the refining is carried out. Thus, a good quality of crude gasoline distillate may be refined to pass the corrosion and Doctor tests with only 2 or 3 lbs. of chlorine in the form of hypochlorite per 1000 gal., but complete desulfurization of a gasoline, such as that from Persian crude, requires about 1 lb. of chlorine per 50 gal.

REFINING OF CRACKED DISTILLATES

It is probable that labil sulfur compounds in oils that have been treated by sulfuric acid are responsible for discoloration when such oils are permitted to stand; this is particularly true of gasoline which has been made by thermal cracking methods and which has been refined by sulfuric acid. When small proportions of sulfuric acid are employed for treating such cracked gasoline, it is possible to bring about a substantial increase in the sulfur content, the sulfur thus introduced being in the form of alkyl esters of sulfuric acid, formed according to the equation—using amylene as an example—



$$2C_5H_{10} + H_2SO_4 \longrightarrow (C_5H_{11}O)_2SO_2$$

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[5] *Ber.*, **49** (1916), 1344, 1551.

[6] *Ann.*, **403** (1914), 11.

[7] *J. Inst. Petroleum Tech.*, **3** (1917), 229.

[8] The presence of sulfur appears to be an advantage in the case of residuum, which is to be blown by air for conversion to asphalt; sulfur accelerates the process, producing a harder product in a given time.

[9] U. S. Patent 525,811 (1894).

[10] U. S. Patent 723,368 (1903).

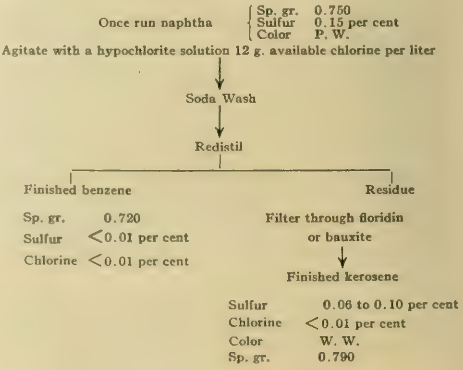
Such esters are not readily removed from the oil by washing with alkali; and it is common experience that such oils, treated in this way, yield free sulfur dioxide when redistilled, even when the alkali wash has been as effective as possible.[11] On the other hand, if large proportions of sulfuric acid are employed for treating, large losses result, varying from about 3 per cent up to 20 per cent, the latter figure being about the average loss on treating Scotch shale oil distillates with sulfuric acid. Very large losses are also experienced in refining crude benzene losses by solution and polymerization frequently amounting to 20 per cent. However, it is now very generally recognized that simple olefins are not objectionable as constituents of motor fuel. It has accordingly become the almost universal practice to refine such cracked naphthas with a small proportion of acid and then redistil to free the gasoline of the sulfuric esters and polymers formed by the acid.

The total loss on refining cracked gasoline, however, is always greater than the observed loss of volume, since a large proportion of the unsaturated hydrocarbons are polymerized to higher boiling hydrocarbons. (When such cracked distillates are not redistilled they quickly become discolored on standing, even for a comparatively short time, and frequently develop a brown sediment and a strongly acid reaction.) This procedure obscures the actual total loss of gasoline. Since polymerization is the principal result with unsaturated hydrocarbons above hexylene in the olefin series,[12] the polymerization loss on treating cracked gasoline is always greater than the observed solution loss. Thus, a cracked gasoline giving a solution loss of 3 per cent will have a polymerization loss of *at least* an equal amount, or a total gasoline loss of at least 6 per cent. This point is worth emphasizing, because it is by no means universally recognized to be a fact. A number of cracked gasolines made by distilling Oklahoma fuel oil under 100 to 150 lbs. pressure showed polymerization losses of 15 to 30 per cent and the dry point was not reached at 260° C. (500° F.). Although these particular gasolines contained a higher percentage of unsaturated hydrocarbons than commercial cracked distillates made to-day, and were treated with more acid, they do demonstrate that such losses are very real and may be comparatively large. This is still further demonstrated by the action of ordinary concentrated sulfuric acid, 66° Bé., on a mixture of amylenes and hexylenes at $-5°$ C., in which case the loss by solution in the acid was only 11 per cent, but 75 per cent of the mixture was converted into high boiling polymers. Small proportions of acid may bring about a very extensive polymerization. Thus, a pure olefin, $C_{12}H_{24}$, of known purity, showed a loss to 85 per cent sulfuric acid of only 4.4 per cent and was almost entirely polymerized; ordinary 96 per cent acid gave a loss of about 10 per cent, and the remainder was *completely* polymerized. The highest solution losses occur in the lighter fractions containing amylenes and hexylenes. In view of the facts just mentioned, it is certain that a careful investigation of the polymerization losses in the present American practice, of refining cracked gasoline by sulfuric acid and redistilling, are very real and probably amount to 3 to 6 per cent of the gasoline treated. The refining of such cracked gasolines by filtering through fuller's earth or similar material also is known to effect some polymerization, and therefore loss, but treatment in this manner has not been very successful or widely adopted. The only published data bearing on this are those of Gurwitsch[12] who noted that amylene was rapidly polymerized by fuller's earth. The refining of such cracked gasoline, including the removal of sulfur compounds, by hypochlorite solutions is by far the most economical method of refining such products.

That the hypochlorite method of refining petroleum distillates had not been worked out many years ago is probably due to the fact that the first attempts resulted in introducing chlorine into the oil. The natural conservatism surrounding a long-established process (sulfuric acid and soda refining), together with the fact that only in recent years has liquid chlorine become a really cheap, bulk staple of the chemical industries, have also been factors in retarding the development and adoption of the new method. Special methods for the cheap and safe transportation of liquid chlorine have also been developed—i. e., specially designed tank cars—and consequently liquid chlorine has rapidly been replacing bleaching powder among consumers of large quantities of bleach.

The active agent in the new process is probably hypochlorous acid. As originally carried out, the hypochlorite solution was generated by the partial electrolysis of salt in specially designed hypochlorite cells. This is unsatisfactory on account of the low utilization of salt, cost of current, rapid deterioration of the cells, and other difficulties which have been the common experience with such cell installations, and the hypochlorite solution is better made up from liquid chlorine, which greatly simplifies the operation and necessary supervision.

The sulfur derivatives in petroleum distillates are rapidly oxidized by dilute hypochlorite solutions, 2 hrs. being the time allowed in the case of the Persian distillates. A concentration of 12 to 15 g. of available chlorine per liter is employed and agitation is accomplished by circulating the aqueous solution through centrifugal pumps discharging below the surface of the oil. The agitators are iron and are not lead lined, experience having shown that corrosion of the iron agitators does not proceed beyond a slight filming of the metal. Part of the sulfur is removed in the form of oxidation products soluble in water. The best procedure, when it is desired to eliminate the sulfur, is to refine the crude naphtha distillate containing both the gasoline and kerosene, then steam-distil the gasoline and pass the kerosene residue through a filter containing dehydrated bauxite or similar adsorbing material to remove the slight color. The oxidized sulfur compounds are much more readily removed by the bauxite than in their original condition. The combined losses amount to about 0.5 per cent in the case of Persian oil, and the refining losses on the same oils as formerly treated by sulfuric acid were 3 per cent. The spent hypochlorite solution is practically a 1 per cent solution of calcium or sodium chloride, and can be disposed of without causing stream pollution or other nuisance. This procedure thus avoids the recovery of acid, burning the acid tars, or other troublesome methods of caring for the acid wastes involved in the old sulfuric acid process.



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[11] Brooks and Humphrey, *J. Am. Chem. Soc.*, **40** (1918), 822.

[12] *J. Chem. Soc. (London)*, **1915**, 933.

When gasoline only is to be treated, the filtering operation may, of course, be dispensed with. The foregoing is an outline of the process as carried out on the distillate from Persian oil. The purification is so effective that with gasoline from Persian oil, containing originally the percentage of sulfur indicated above, the regular commercial output passed the following tests:

1—100 cc. gasoline + 1 cc. $KMnO_4$ 0.1 N soln. + 2 cc. 10 per cent sulfuric acid, and vigorously shaken retains the permanganate color for 10 min., usually much longer.

2—When a sample of the gasoline is treated with sodium and alcohol and, after the reaction is over, slightly acidified and tested with lead acetate, no film of lead sulfide can be detected.

3—The copper dish test is entirely negative.

4—The Doctor test is negative

The Composition of Erythrosin[1]

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Although tetraiodofluorescein was discovered in 1875, the commercial purification of its sodium salt was not well understood even in 1909, as is evidenced by the statement of E. G. Kohnstamm[2] before the Seventh International Congress of Applied Chemistry in that year: "Of twelve samples of erythrosin examined, ten were not erythrosin at all, and of the other two, one was low in iodine, and one contained arsenic." To-day, with the dyestuff standing as one of the seven permitted food colors and receiving important consideration as a sensitizer of photographic plates, the subject of its preparation has attained considerable importance. When intended for use as a food color, it is obviously necessary to place the requirements in regard to purity as near the theoretical as technical practice will allow. The failure, however, of carefully made and apparently pure technical erythrosin to conform to the standards set by the United States Bureau of Chemistry[3] has made it seem doubtful if the formula $C_{20}H_6O_5I_4Na_2$, as given in Schultz's *Farbstofftabeln* for 1914, page 200, and as adopted by the Bureau of Chemistry, is correct.

In this communication are submitted the results of a study concerning: (*a*) the preparation and purification of tetraiodofluorescein, (*b*) the conversion of this into the sodium salt—i. e., erythrosin, (*c*) the composition of pure erythrosin, and (*d*) the composition of the technical product.

Preparation of Tetraiodofluorescein

Fluorescein was prepared in the usual manner from phthalic anhydride, resorcinol, and zinc chloride, and was carefully purified. Its purity was further confirmed by converting a portion into the diacetate, and this was found to melt at 199° to 200° C.[4]

Three methods are described in the literature for the preparation of tetraiodofluorescein: (1) the electrolysis of an alkaline solution of fluorescein containing a little excess of iodine;[5] (2) the treatment of a comparatively cool alkaline solution of fluorescein and sodium iodide with ammonium or potassium persulfate;[6] and (3) direct halogenation in hot dilute acetic acid with an excess of iodine.[7] For laboratory preparation this last method seemed to offer the best possibilities.

Twenty-four grams of fluorescein were dissolved in a hot mixture of 24 cc. of 30 per cent sodium hydroxide and 240 cc. water. One hundred grams of iodine and 240 cc. of water were treated with just sufficient 30 per cent sodium hydroxide solution (105 cc.) to cause decolorization, and the two solutions were mixed and heated nearly to boiling. One hundred grams of glacial acetic acid were allowed to flow in drop by drop, with good stirring, the temperature being maintained at nearly the boiling point. The liquid was then partially neutralized with 55 cc. of the sodium hydroxide solution, and, after short standing, made strongly acid with 200 cc. of 1:1 hydrochloric acid. After boiling for a minute, the mixture was diluted with hot water to 3 liters, and the whole allowed to stand for several hours. The yield of crude, amorphous product was 95 per cent.

It was found that the method of Mühlhauser—namely, repeated digestion with dilute hydrochloric acid—did not remove all the adhering iodine. Treatment of an alkaline solution of the dye with sodium sulfite apparently removed some of the halogen even from the molecule itself. Repeated digestion with sodium iodide gave a product very light in color, but which still retained some iodine, as could be demonstrated by heating the acid at 135° C., whereupon vapors of iodine were given off. Treatment with 5 per cent sodium thiosulfate solution was not efficient, and there always resulted a slight precipitate of sulfur. The following procedure was finally adopted for securing a product which, while amorphous, was free from occluded and adsorbed iodine: four washings of the crude substance with water containing a little sulfuric acid in order to repress the solubility of the iodo compound, two extractions with warm alcohol, then solution in dilute sodium hydroxide (50 g. dye in 3 l. of water), and precipitation, hot, with dilute sulfuric acid; then again washing with water, and finally with alcohol. The final product was very light in color and did not give off iodine vapors when heated for one hour at 150° C.

The product thus purified, while entirely free from occluded iodine, contained about 6 per cent of diiodofluorescein, as was evidenced by its iodine content—59.74 instead of 60.75 per cent. It is almost impossible to separate completely the tetraiodo from the diiodo compound by recrystallization of the mixture of the acids, because the two are nearly alike in respect to solubility, or rather insolubility, in the usual solvents. Nor can one depend upon the melting point as a criterion of purity, for this is very indefinite. In order to obtain perfectly pure tetraiodofluorescein, we have therefore converted our product into the diacetate, purified the latter by recrystallization until the melting point was constant and iodine analysis indicated a compound of unques-

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[1] Received May 8, 1922.

[2] *Proc. 7th Internat. Cong. Appl. Chem.*, **1909**, Sec. 4*b*, p. 122.

[3] "Coal-Tar Colors Used in Food Products," *U. S. Dept. Agr., Bull.* **147**, 206.

[4] Baeyer, *Ann.*, **183** (1876), 2, 13.

[5] *Chem. Zentr.*, **1900**, **II**, 1176. Société chimique des Usines du Rhone, Anct. Gilliard, P. Monnet, et Cartier, D. R. P. 108,838.

[6] Winther, "Patente der Organischen Chemie," **2** (1877–1905), 169.

[7] Mühlhauser, *Dinglers polytech. J.*, **263** (1886), 99; **283** (1892), 258.

tioned purity. This diacetate upon saponification gave us the pure tetraiodofluorescein.

TETRAIODOFLUORESCEIN DIACETATE—25 g. of tetraiodofluorescein, 100 cc. of acetic anhydride, and 5 g. of fused sodium acetate were heated in an oil bath under a reflux condenser for 2 hrs. at 150° C., and the solution was then poured while still hot into ice water. The solidified mass, washed with water and dilute sodium hydroxide, and dried, was recrystallized from boiling bromobenzene. It then became soluble in cold acetone, from which, however, it almost immediately reprecipitated as a beautifully crystalline white powder, nearly insoluble in all solvents of low boiling point. By three crystallizations from bromobenzene, alternated with the above-mentioned solution and precipitation from acetone, a pure white product was obtained which melted at 293° to 294° C. Yield, 14 g.

Calculated for diacetate $C_{24}H_{12}O_7I_4$: I, 55.20 per cent.
Found. I, 55.27, 55.46, 55.08; 54.90. Av. 55.18 per cent.

SAPONIFICATION OF THE DIACETATE—Of several methods tried, the following was found most suitable: 10 g. of erythrosin diacetate were suspended in a mixture of 600 cc. of acetone, 45 cc. of water, and 90 cc. of ammonium hydroxide solution at room temperature for 8 to 10 hrs., complete solution having been effected in about one-third of this time. The filtered solution was diluted with one-fourth its volume of water and, after partial neutralization with dilute acid, heated to 40° to 50° C. Upon complete acidification, pure acid precipitated crystalline. In this condition the air-dried material retains only 0.5 per cent of solvent. Yield, 95 per cent. The acid purified through the diacetate could readily be obtained in crystalline form even from its warm aqueous ammoniacal solution by dilute acetic acid, complete separation being insured by finally adding a little sulfuric acid. The same material precipitated in the cold was amorphous, but when sufficiently washed was equally pure.

				Per cent			
Calculated for $C_{20}H_8O_5I_4$:		I,		60.75			
Found: Lot 1		I,	60.44	60.51	60.67	Av. 60.54	
Lot 2		I,		60.62			
Lot 3	Hot pptn.	I,	60.43	60.27	60.73	Av. 60.54	
	Cold pptn.	I,	60.65	60.56	60.65	60.81	Av. 60.67

Tetraiodofluorescein thus prepared is insoluble in all the usual solvents which boil below 100° C., with the exception of alcohol and moist acetone, and only slightly soluble in these. Ethylene chlorobromide and dibromide dissolve a little on heating, as does bromobenzene, but the precipitates obtained on cooling are not fully crystalline. The solubility in ethyl salicylate is low. Nitrobenzene dissolves 1 g. per 15 cc. at 160° C., but at best only half of this is precipitated on long standing, and the product is somewhat low in iodine content. *m*-Cresol proved an unusually good solvent at its boiling point, but here again the yields were never better than 50 per cent and the product analyzed only 59.37 per cent iodine.

METHOD OF IODINE ANALYSIS—For the determination of the percentage of iodine, the Pringsheim method, fusion with sodium peroxide, proved entirely unsuitable. The chromic acid oxidation according to Baubigny and Chavaunne[8] was applicable and has been used to some extent, but the results were inferior in constancy to those obtained by the method of Seeker and Mathewson,[9] as is shown on the same sample in both cases, in the following table:

	Per cent Iodine
Baubigny and Chavaunne	50 09; 47.89. 48.29; 48.09
Seeker and Mathewson	48 90; 48.99; 48.94

Some slight modification of the second method, however, was found advisable, especially in the case of acid dried for a long time. 0.2 to 0.3 g. of tetraiodofluorescein was dissolved in 20 cc. of water and 10 cc. of 10 per cent sodium hydroxide by heating gently for a few minutes. (With the sodium salt, only 2 cc. of sodium hydroxide are necessary.) While still hot, 40 to 60 cc. of a saturated solution of halogen-free potassium permanganate were added, followed by 12 to 15 cc. of concentrated nitric acid. The subsequent treatment was identical with that given by Seeker and Mathewson. It was found that this method of halogen estimation could be applied to the diacetate also, if the sample were dissolved in 30 cc. of 70 per cent alcohol and 15 cc. of 10 per cent hydroxide, and heated on the water bath until all alcohol was removed and saponification was complete before the addition of permanganate and nitric acid.

PREPARATION OF ERYTHROSIN

For the preparation of the disodium salt of tetraiodofluorescein, a suspension of the acid in water could be exactly neutralized by the addition of the requisite amount of standard 0.02 *N* alkali and the solution evaporated to dryness. It was found, however, that products obtained in this manner were difficult to get dry and were invariably low in iodine. Sodium carbonate gave us better results, and accordingly the following method was adopted: 3 g. of tetraiodofluorescein and an equal weight of dry sodium carbonate were suspended in 150 cc. of absolute alcohol and, after standing some hours, the whole heated to boiling for a few minutes. The undissolved carbonate was filtered off and the liquid concentrated under reduced pressure until the separation of the salt commenced. The small amount of precipitate was removed by filtration and the evaporation of the solution continued further. When the volume had reached approximately 30 cc., an equal amount of absolute ether was slowly added and crystallization allowed to proceed over night. The red crystals were separated rapidly by filtration, washed with alcohol and ether, and dried in a vacuum desiccator over fresh sulfuric acid. Erythrosin prepared as described contains solvent of crystallization which, however, is not all alcohol, but in part water. The water has partially resulted from the neutralization of the erythrosin acid by the sodium carbonate, and in spite of the fact that the amount of water is exceedingly small as compared with the large amount of alcohol, nevertheless erythrosin takes up that water, so great is the avidity of the sodium salt to form a hydrate. Completely hydrated erythrosin is obtained when the pure sodium salt, freed from alcohol by drying at 130° C., is dissolved in water, the solution evaporated to dryness under reduced pressure, and the dry residue further dried in a vacuum desiccator.

PURE ERYTHROSIN

In the following table are given the results of analyses of several samples. The relative proportions of alcohol and water in erythrosin were obtained as follows: A weighed sample of the salt (3 to 4 g.) was put in a large boat, placed in a glass tube and heated at the desired temperature, a stream of air carrying the vapors into a combustion tube. From the quantities of carbon dioxide and water produced, the relative amounts of the two solvents in the sample of erythrosin can be calculated. All samples, whether from alcohol or from water, were dried, prior to analysis, over sulfuric acid in a vacuum desiccator for 2$^1/_2$ to 3 hrs., which period should be amply sufficient to free crystalline material from any adhering volatile solvent.

These results indicate clearly that erythrosin combines with both alcohol and water. The actual number of mols of each of the two solvents per mol of dye could only be determined approximately, since in the initial stages of dry-

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[8] *Chem. Zentr.*, **1903**, II, 69; **1904**, I, 609; **1908**, I, 2111.

[9] *Chem. News*, **103** (1911), 161.

No.	Solvent	Preliminary Drying in Vacuum Desiccator at Room Temp.	Heated Temp. °C.	Hrs.	Loss, Per cent Alcohol		Water	Per cent
1	Alcohol	10 hrs.	Room	10	..	1.10	..	..
			120–130	1	..	7.01	..	..
			130	4	..	0.09	..	8.20
2	Alcohol	4 days	125	9	2.50	..	1.02	
			170	4	0.14	..	0.39	4.05
3	Alcohol	4 days	170	4	[illegible].85	..	1.67	4.52
4	Water	2½ hrs.	Room	9	.	..	1.02	..
			130	1	.	..	5.23	.
			130	3	.	..	0.48	.
			160	16	..	..	0.32	7.05

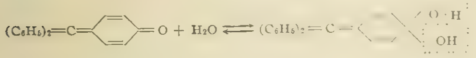
ing in the desiccator, some of the solvent is undoubtedly lost. Approximately, from water the salt contains: 1 mol erythrosin + 4 mols H_2O; from alcohol, 1 mol erythrosin + 2 mols C_2H_6O; from alcohol containing but a very little water, some of each solvent is taken up. But whatever the composition of the hydrated salt, it is obvious that in drying the last portion of the water is retained with extreme tenacity. The question arises—what assurance does one have, outside of the analysis of the dried salt, that all the water has been driven out even when the salt is heated for hours at 160° to 170° C.? May not a state of equilibrium be established at that temperature, wherein liberation of water from the salt proceeds at a very slow rate? Much higher temperatures for drying are inadvisable, for decomposition of erythrosin is likely to set in, evolution of iodine becoming quite noticeable at 200° C. We have analyzed Sample 3 after it had received the treatment described—namely, 4 hrs. at 170°, and Sample 4, which had been dried 5 hrs. at 130° C. and 16 hrs. at 160° C. The results in per cent iodine are:

Sample 3	57.10	56.84	57.01	Av. 56.98
Sample 4	57.20	56.80		Av. 57.00

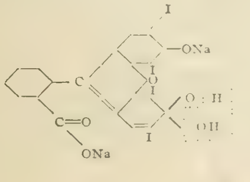
Calculated for $C_{20}H_6I_4O_5Na_2$: 57.70; $C_{20}H_6I_4O_5Na_2 + H_2O$: 56.55

That the long heating in the process of drying the two samples at the temperature recorded did not induce decomposition of erythrosin with possible loss of iodine, is evident from the fact that the acid regenerated from the salt was found to contain the right amount of iodine—viz., 60.51 against 60.75 per cent calculated. The conclusion, therefore, seems to be that the low iodine content—approximately 57.00 instead of 57.70 per cent—of our erythrosin, which had been prepared from very pure acid and had been thoroughly dried, must be due to the retention of water by the salt to the extent of about 1.2 per cent (calculated for 1 mol H_2O, 2.00 per cent).

With regard to the manner in which the water is held, little may be said with certainty. In a series of papers from this laboratory, it has been shown that diphenyl fuchsone and many analogous compounds possess the tendency to combine with water and give rise to quinonoid tautomers of the carbinols of varying degrees of stability.



Erythrosin, on the basis of its constitution and in analogy with the other and simpler fuchsones, may act in a similar manner. The constitution of the salt, then, is as follows:



Technical Erythrosin

A sample of commercial erythrosin acid of reliable manufacture was subjected to the same analyses as our sample which had been completely purified through the diacetate. The acid, upon digestion with alcohol, was found to be practically free from adsorbed iodine. Dried in a vacuum desiccator and for a few minutes at 130° C., it contained 60.61 per cent of iodine against the theoretical 60.75. The acid was converted into erythrosin, in absolute alcohol with sodium carbonate, just as described for our own sample, and the resulting salt was dried in a vacuum over sulfuric acid at room temperature.

(1) One portion of this erythrosin, which had been dried at room temperature for 12 hrs., was heated at 120° to 130° C., and it lost in alcohol and water, during the first hour and a half, 6.27 per cent, and during the next 4 hrs., 0.3 per cent.

(2) A second portion was recrystallized from water, and the sample, after 13 hrs. in a vacuum desiccator, lost at 130° C., during the first hour, 5.65 per cent, and in the next 3 hrs., 0.36 per cent; after that in 16 hrs. at 160° C., 0.09 per cent.

(3) A third portion, from alcohol, lost in 11 hrs. at 135° C., 7.36 per cent as alcohol and 1.36 per cent as water.

(4) A fourth portion, also from alcohol, lost in 4 hrs. at 170° C., 7.57 per cent as alcohol and 1.2 per cent as water. Now, just as in the case of our own erythrosin, this technical product, in spite of the drastic treatment, did not apparently lose all its water. Here again the salt contained less iodine than it should if it were completely dehydrated. Sample 4 gave 57.27, 57.14, 56.92 per cent; average, 57.09 per cent iodine.

Conclusion

The conclusion seems justified that the true composition of erythrosin is $C_{20}H_6I_4O_5Na_2 + H_2O$, and that it is almost impossible to dehydrate it completely without risk of decomposition of the salt. In view of this, we suggest that the specifications of purity be based upon the following principles: (1) Erythrosin should be dried to approximately constant weight at 120° to 125° C., weighings being made at the end of the second hour and every hour thereafter; it should, then, on solution in very dilute ammonia and careful precipitation, hot, with acetic acid followed by a little sulfuric acid, give 93.5 ± 0.5 per cent of its weight of dry erythrosin acid, after adding a correction of 0.4 per cent for each 100 cc. of water used with a 1-g. sample. This solubility correction was found necessary in experiments upon pure erythrosin acid. (2) The precipitated erythrosin acid should give up no iodine to alcohol, and should, when dry, contain about 60.75 per cent of iodine.

Fire Hazards in Oil Refineries

Fires in oil refineries may be caused by lightning or other mishap, or by carelessness in allowing the oil or vapors to become ignited, states the Bureau of Mines in Serial 2400 just issued. Probably the most frequent cause, however, is the failure of refining equipment. Stills are designed to be safe, and usually are safe. Nevertheless, defects sometimes occur, as in all metal structures, and unless promptly discovered and remedied may result in serious fires and explosions. The dangers of refining crude oil are well recognized, and all modern refineries have developed highly efficient systems of inspection and fire prevention.

Further tests have been conducted at Pittsburgh, Pa., by the Bureau of Mines to obtain data as to the comparative sensitiveness of gasoline vapors and methane with respect to their ignition from electric flashes. This work has a bearing on the degree of protection that will be necessary for electric motors used in and around buildings where gasoline vapor may be present.

The Manufacture of Hydrogen by the Partial Liquefaction of Water Gas and Coke-Oven Gas[1,2]

By Georges Claude

Société de Grande, Paroisse, near Montereau, France

FOR A NUMBER of years already I have been engaged in the manufacture of hydrogen by the partial and direct liquefaction of water gas and its analogues. For this purpose water gas, compressed to a suitable degree, is in the first instance deprived of its carbon dioxide and is dried. The gas is then sent into a heat exchanger, E (Fig. 1), in which it is cooled by circulating in the opposite direction to the hydrogen and carbon monoxide which have already been separated. The gas then enters, by the collector C, the bottom of a sheaf of vertical tubes, F, the lower portion of which plunges into a bath of carbon monoxide boiling under atmospheric pressure. By the combined influences of the pressure and of the temperature of the liquid bath, a large portion of the carbon monoxide of the ascending gases is liquefied; it flows back into the collector C. Owing to the pressure this liquid is forced out through the tube T and the cock R, into the vaporizer V, where it replaces the liquid which is being evaporated. The remaining gas, containing hydrogen and a little of the residual CO, continues to rise in the sheaf of tubes F. There the gases encounter a temperature which is more and more being lowered, by means which I shall presently explain. Under that influence the rest of the carbon monoxide is liquefied. *Theoretically*, therefore, it is a sensibly pure hydrogen which escapes from the top of the tubes, and it is this cold and compressed hydrogen which is expanded in the nozzle D, and further cooled by this expansion to be sent back around the sheaf F, in order there to produce the very low temperatures of which I have just spoken.

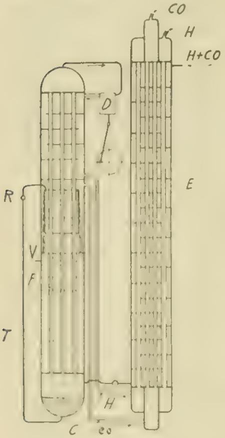


FIG. 1

In working this process two sources of inconvenience were experienced which I have only recently been able to overcome. In the first instance, when the hydrogen is arriving at extremely low temperature in the nozzle, as indicated, the frigorific efficiency of the expansion will be very low. There is in that case a "loss" of liquid, unless we go up to pressures regrettably high from the point of view of energy expenditure and this all the more so because none of the customary lubricants can be employed at these temperatures. Hence there is abnormal friction in the nozzle which will again lower the frigorific efficiency. In the second instance, the calorific mass of the gases leaving the tubes, and afterwards the nozzle D, and circulating about the rising gases, will be smaller than that of the latter by the whole mass of the carbon monoxide which had been liquefied by their action. As a consequence the ascending gas cannot, even assuming a perfect heat exchange to take place, leave the sheaf of tubes at the temperature at which the expanded gases entered the tubes. The final temperature of the expansion of hydrogen will, therefore, not be very low, and in addition this temperature will be badly utilized for the purification of the ascending gases.

These various troubles have been overcome in the following manner:

1—Part of the compressed gas which is entering the system is withdrawn from the heat exchanger E, at a point, M (Fig. 2), before it arrives in the cold portion; it is thus relatively little cooled. It is sent through the tube *t* into an auxiliary system of tubes, G, around which the hydrogen, leaving the bundle and passing on to the nozzle, is being circulated by means of the pipes L and K. This relatively warm gas will then reheat the hydrogen before its expansion and will hence increase the efficiency of the expansion process.

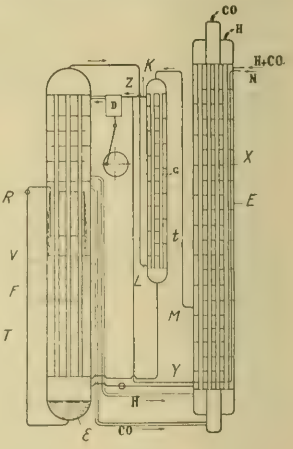


FIG. 2

2—If we relied exclusively upon this means, the final temperature of the expansion would remain bad owing to the want of lubrication and to the eventual freezing out of the residual CO (−206° C.). We must manage to lubricate the machinery by a substance which will remain liquid when the temperature sinks below −206° C. That body cannot be petrol ether, or some similar substance, since they would all be solidified at this temperature. I have, therefore, made use of nitrogen which only solidifies at −211° C., and which can, moreover, be added to the hydrogen before its expansion without causing any complication, at least in cases when we are aiming at the synthesis of ammonia. A current of compressed and dried nitrogen is cooled down to about its condensation point in the heat exchanger E by means of the tube system XY; it is then added to the hydrogen at Z, before the hydrogen enters into the nozzle. In this way then we secure acceptable conditions for the lubrication. As a first consequence, the temperature of the escaping gas is easily lowered down to −208° and −210° C., as soon as we lubricate by means of nitrogen. As a second consequence, this addition of nitrogen to the gases leaving the tubular system increases, to any extent that we desire, the calorific mass of the expanded gas. The latter gas may therefore equal or surpass in mass that of the gas ascending in the sheaf F, including the carbon monoxide which has been condensed in this part of the tubes. As a result the temperature of expansion is considerably improved, and it is moreover much better utilized. We can, indeed, easily eliminate by these means the carbon monoxide within 1 per cent, and the hydrogen finally isolated can without

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[1] A contribution to a general discussion on "The Generation and Utilization of Cold," held by the Faraday Society and the British Cold Storage and Ice Association, October 16, 1922. Reprinted by permission of Faraday Society.

[2] Translated by H. Borns.

any difficulty be used in my *hypercompression* process for the synthesis of ammonia.

This process has been developed and put into practice in the works of the Grande Paroisse, near Montereau, where an apparatus for the production of 500 cu. m. of hydrogen per hour is in operation, feeding a unit for 5 tons of ammonia per day. The carbon monoxide containing all the nitrogen of the water gas, it should be noted, is discharged at a percentage which may easily be raised to 85. The hydrogen efficiency is therefore excellent. The carbon monoxide may be utilized either for the manufacture of various chemical products or for driving the internal combustion motors of the installation.

The process which I have outlined requires the compression of the gases to degrees varying with the size of the apparatus from 15 to 30 atmospheres. The first figure applies to apparatus of a capacity of 2000 cu. m. of hydrogen per hour. This process necessitates the command of a relatively high motive power, and one might draw attention to the advantages offered by processes based upon the catalysis of CO into CO_2, such as are, for instance, employed in the Haber process. I have, therefore, studied and tried this process only with a view of its ulterior application to a particularly interesting case—that of the *coke-oven furnaces*, in which the presence of a considerable portion of methane renders catalytic processes inoperative. The complexity of the gas mixtures we have to deal with in this case and the diversity of the freezing points of the constituents might make us fear that we should have to meet serious difficulties in the working of this process. As a matter of fact, however, an apparatus has already been constructed for this purpose and has, after very short trials, been put successfully to service in the Béthune mines. The essential cause of the success is the very high reciprocal solubility of the diverse condensable constituents. This first apparatus has a productive capacity of 350 cu. m. of hydrogen per hour, and it is operating with a compression of about 25 atmospheres. An installation for the utilization of the hydrogen produced by means of this apparatus in the manufacture of ammonia by the application of hyper-compression has already been erected and is actually being put in working order. I hope that this installation will be the point of departure for a much more important installation in which I intend to make use of apparatus for the production of 2000 cu. m. of hydrogen per hour.

One of the essential reasons that make me count upon a development of this process in the coke-oven industry lies in the multiple indirect advantages which the process promises.

On the one hand, since the gases to be treated must already be compressed for the extraction of the hydrogen, we are naturally led to effect the stripping of the gas of its benzene likewise *under compression*. All the benzene, which at present escapes when the process is carried out at atmospheric pressures, will then easily be retained; that will constitute a gain which in certain cases may come up to 1 kilogram of benzene per ton of coke. This improved recovery will, moreover, be attained by means of an infinitely reduced amount of solvent and of heat energy, and at much diminished losses of solvent. The recovery will be effected in absorption and distillation apparatus of comparatively very small dimensions. On the other hand, the ethylene, this precious gas the percentage of which in furnace gases is too low for its successful extraction at atmospheric pressure, may easily be collected to a large extent in the course of the operations. For it will be condensed almost alone in the preliminary cold-exchanger of the apparatus, and it can be extracted as a 40 or 50 per cent mixture which will very readily be utilizable, either for the manufacture of alcohol or for use in autogenous welding or similar apparatus. To give an idea of the possible importance of this by-product, I may state that, supposing the furnace gas is treated to contain 1.5 per cent of ethylene and that it can all be extracted—that would correspond to our obtaining 200 liters of alcohol per ton of ammonia in addition to other products.

Finally, I should remark that, from the calorific standpoint, hydrogen must be regarded as the very worst of all combustible gases. One cubic meter of hydrogen represents only about 2600 calories (lower calorific power) against the 3000 calories of carbon monoxide and the 10,000 of methane. When we, therefore, extract the hydrogen from coke-oven gases, we, in fact, enrich the gases in a true sense, and it is a considerable enrichment which they undergo, since they become fit for uses for which they would otherwise be unsuitable. When the gas is to be distributed, it will be free of every trace of the condensable impurities that cause so much mischief in our actual gas distribution systems; when it is to be utilized as industrial gas, it will enable us to obtain extremely high temperatures and to combine, under specially interesting conditions, the production of nitric oxide by the Häusser process with the synthesis of ammonia.

These are the principal advantages of the process which I have the honor to describe before you. I should like to emphasize that one of the characteristic essential features of the process is the extreme smallness of the necessary apparatus. An apparatus for 1000 cu. m. of hydrogen per hour requires a sheaf of liquefaction tubes 40 cm. in diameter and 3 m. in height.

Lectures at Naval Academy

The lectures by members of the AMERICAN CHEMICAL SOCIETY before the Naval Academy at Annapolis, Md., have again been arranged for 1922–1923. The officers of the Navy have expressed most cordial appreciation of the efforts which the AMERICAN CHEMICAL SOCIETY has been making to see that they are supplied annually with instructive chemical information from some of its prominent members. The lectures given for the present year are as follows:

OCTOBER 21 AT 11 A.M.—"The Role Played by Cellulose in the Late War," by Prof. Harold Hibbert, Yale University, New Haven, Conn.

NOVEMBER 18 AT 11 A.M.—"The Economic Independence of the United States," by Dr. Edwin E. Slosson, Head of Science Service, 1115 Connecticut Ave., Washington, D. C.

DECEMBER 9 AT 11 A.M.—"Nitrogen Fixation and Its Relation to the Production of Food and Explosives," by Prof. A. H. White, University of Michigan, Ann Arbor, Mich.

JANUARY 13 AT 11 A.M.—"Chemistry as a Key to International Relations," by Mr. H. E. Howe, Editor of *The Journal of Industrial and Engineering Chemistry*, 810 Eighteenth St., Washington, D. C.

JANUARY 27 AT 11 A.M.—"Use of Chemical Agents in Warfare," by Major E. J. Atkisson, Edgewood Arsenal, Edgewood, Md.

FEBRUARY 17 AT 11 A.M.—"Helium, Its History, Properties, and Use in Aeronautics," by Dr. R. B. Moore, Chief Chemist, Bureau of Mines, Washington, D. C.

MARCH 17 AT 10.30 A.M.—"The Chemical Control of Gaseous Detonation with Particular Reference to the Internal Combustion Engine," by Mr. Thomas Midgley, Jr., General Motors Research Corporation, Dayton, Ohio.

Platinum Theft

During the past summer platinum thieves twice visited the State University of Iowa. On the first occasion two platinum crucibles with their covers were stolen from the physical laboratory, and on the second a desk in the analytical laboratory was broken open and several crucibles and their covers taken. A further unsuccessful attempt was made between November 4 and 6, 1922, when a desk was forced open and an effort made to open the safe in the storeroom. The university has not yet succeeded in tracking down the thieves.

The Measurement of the Plasticity of Clay Slips[1,2]

By Robert E. Wilson and F. P. Hall

Research Laboratory of Applied Chemistry, Massachusetts Institute of Technology, Cambridge, Mass.

The paper emphasizes the great need of a quantitative measure of the physical properties commonly included in the term "plasticity" of clays and clay slips. Various indirect methods previously suggested are likely to lead to erroneous conclusions, while measurement of the flow or apparent viscosity of clay slips made up with a constant amount of water is shown to give misleading results.

The work described in this paper is preliminary in nature, and has been confined to a study of the properties of clay-water mixtures in the casting rather than in the molding range. In the light of these results, it is recommended that, instead of the vague term "plasticity," the properties of a given clay, at least for casting purposes, be expressed in terms of (a) the water content required to give proper working consistency, and (b) the resistance of the resulting slip to small deforming forces—such as gravity. Specifically, use is made of a modified Bingham plastometer, and the figures reported are: (a) the amount of water required to give a slip of a specified mobility, and (b) the yield value of the slip thus obtained.

The method is shown to be capable of giving quantitative figures for the yield values at constant mobility which correspond well with the customary qualitative ideas as to the plasticity of clays. The amount of water required to give constant mobility varies to a surprising extent, and does not seem to bear any definite relationship to the usual classifications of more and less plastic clays. It probably does parallel fairly well the shrinkage or drying.

Small amounts of acid or alkali are shown to have a negligible effect on the mobility of a clay slip but a very large effect on the yield value, the variations being greater than the difference between a nonplastic kaolin and a highly plastic ball clay. This brings out the necessity, and indeed the potential value, of carefully controlling the hydrogen-ion content of the water used in making the slips.

Some preliminary data are given on the effect of additions of flint and similar nonplastic materials to clay slips.

It is recommended that an attempt be made to agree upon standard dimensions for the capillary and the desirable mobility for various purposes, and that the plastometer then be used as a standard method of test in the ceramic industry.

From a practical standpoint, "plasticity" is one of the most important properties, or rather combination of properties, possessed by any clay. Different clays are known to vary greatly in plasticity. Furthermore, in practical clay working substances are frequently added for the express purpose of increasing or decreasing the plasticity of the final mix.

In spite of these facts, however, no unit of plasticity has ever been defined, and there is no generally accepted method of measuring or comparing the plasticity of different clays. To be sure, many indirect methods have been suggested for its quantitative measurement—for example, the amount of adsorption of malachite green, the adsorption of alkali from various salt solutions, the strength of clay bodies after drying, the amount of water required to bring the clay to proper consistency, etc., etc. These factors are undoubtedly in some way related to plasticity, being common results of similar causes, the main factors probably being the fineness of subdivision of the ultimate particles and their affinity for water. It is nevertheless true that in many cases clays—e. g., fuller's earth—possess high adsorptive power for dyes, etc., and yet low plasticity. Such indirect methods of measuring plasticity have therefore not met with any general acceptance, and experienced clay workers still place ultimate reliance on empirical tests, although even such individuals do not consistently agree with one another.[3]

It is obvious that the ultimate solution of the problem must involve a measurement of the physical properties of a clay slip with a water content approximately correct for practical use. Some efforts have been made in this direction by determining the flow of a clay slip through an orifice or by the use of paddle wheel viscometers, but these have not given satisfaction, partly because of the difficulty in determining just how much water should be added before making the test, and partly because it is not possible to measure the true viscosity of clay slips, as is evidenced by the subsequent discussion.

The most promising possibility for making the desired measurement is the use of a device such as the plastometer, recently developed by Prof. E. C. Bingham, and well described in *Scientific Paper* 278 of the Bureau of Standards. Professor Bingham has shown that when a plastic substance flows through a capillary of constant dimensions, the amount of flow is not directly proportional to the pressure used, as in the case of viscous liquids, but departs therefrom by giving abnormally low rates of flow for low pressures and then increasing more rapidly at higher pressures. The two different types of flow curve are illustrated very clearly in Fig. 1, which presents results for a very viscous oil and for a clay slip, in the capillary used in the work described in this paper.

It is Professor Bingham's belief that the rounding off in the curve in the lower portion may be due to slippage or seepage, and that the laws of plastic flow may for all practical purposes be represented by a straight line intersecting the abscissa axis at some point to the right of the origin. The

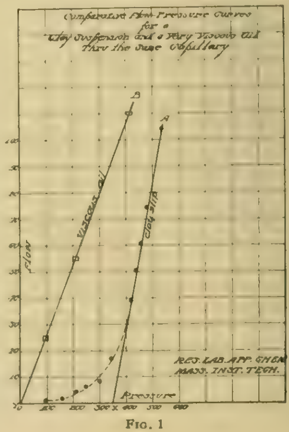

Fig. 1

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[1] Received October [illegible], 1922. Presented before the Division of Physical and Inorganic Chemistry at the New York Meeting of the American Chemical Society, September 6 to 10, 1921.

[2] Published as Contribution No. 63 from the Research Laboratory of Applied Chemistry, Massachusetts Institute of Technology.

[3] This has been strikingly confirmed by a paper by Bole which appeared after this paper had been written—see *J. Am. Cer. Soc.*, 5 (1922), 469.

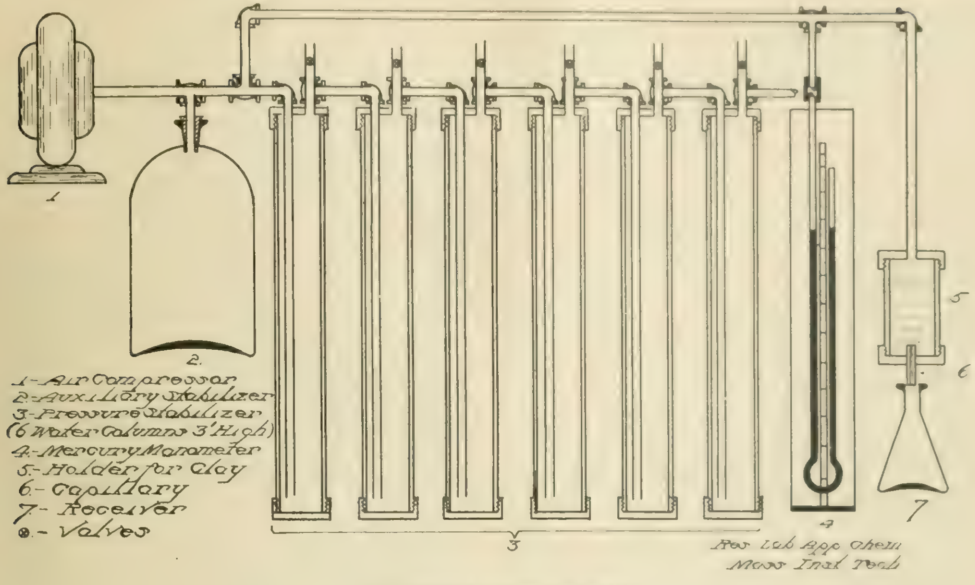

FIG. 2—MODIFIED BINGHAM PLASTOMETER

distance to the point of intersection, in proper units, is defined as the yield value, and the slope of the line is a measure of the mobility of the suspension. It is not the purpose of this paper to discuss the rather involved points with regard to the cause and equation for the lower curved portion of this line, or the questions that have arisen as to the degree of dependence of the results on the size of the capillary used. Both these factors, while of considerable theoretical interest, may for practical purposes be eliminated by agreement upon a standard capillary and by working with proper pressures, just as has been done in practical viscometry by using the Saybolt instrument.

Thus, the reason for the difficulties and apparent contradictions encountered in measuring the "viscosity" of clay slips becomes apparent. The calculation of viscosity from a single flow-pressure observation tacitly assumes that flow is directly proportional to pressure. For example, in the two curves in Fig. 1 a measurement at very high pressure would indicate that the clay slip had a lower viscosity than the oil, while measurements at pressures of 100 or 200 g./sq. cm. would indicate that the clay was more than ten times as viscous as the oil. By determining the complete curves and separating the apparent viscosity into its two components, mobility and yield value, the whole matter becomes clear. An attempt along somewhat similar lines was made by Bleininger and Ross,[4] who measured the flow through an orifice of various clay mixes under variable pressure, but they drew no conclusions as to the significance of the results, or possible ways of measuring or expressing the two separate factors involved.

APPARATUS AND MANIPULATION

The apparatus used was a modified Bingham plastometer, shown diagrammatically in Fig. 2. It consists chiefly of a pressure stabilizer for maintaining constant pressure of several different magnitudes, a container for holding the material to be tested, into the lower end of which is fastened a capillary, and a manometer for measuring the pressure. A general description of the apparatus is given by Bingham in *Proceedings of the American Society for Testing Materials*, 19 (1919), Part II. The flowmeter as described by Bingham and Green was not used in these measurements, but the weight of the discharge and the density of the clay slip were used to determine the volume. The instrument is limited to materials having a very slow "settling time." Furthermore, for very stiff pastes the pressure range must be great enough to permit the linear portion of the curve to be determined.

A number of preliminary trials were made to determine what size of capillary seemed most suitable for use on slips in the casting range. The smaller capillaries, such as used by Professor Bingham, were not found satisfactory in working with clay slips, especially when coarser particles were admixed. When the most suitable capillary was finally selected, its dimensions were carefully determined—the diameter by filling it level with mercury and weighing. It was found to have the following dimensions: length, 5.020 cm.; diameter, 1.3624 mm.

The capillary was later measured at the Bureau of Standards with a high-power micrometer microscope, which gave a figure of 5.021 cm. for the length and 1.3636 mm. for the average diameter.[5] This capillary was used in all the tests discussed in this paper except where otherwise noted.

SOURCE AND TREATMENT OF CLAY SAMPLES

The clays used in these experiments were selected as representative of the clays used in the ceramic industry to-day.[6] The Georgia kaolin is a white-burning clay, free from grit, and with a soapy feel due to the presence of many muscovite scales of microscopic size. The North Carolina clay is a kaolin of residual origin which is used extensively for the manufacture of white ware. The Tennessee ball clay is a very plastic clay of sedimentary character and possesses very good bonding-power. The English ball clay is similar to the Tennessee ball clay. The English china clay is a very lean, white-burning kaolin. Several fire clays were tested, but their history was not known. All except the ball clays were subjected to a washing process before they were used. This is the same treatment that they receive before being put on the market.

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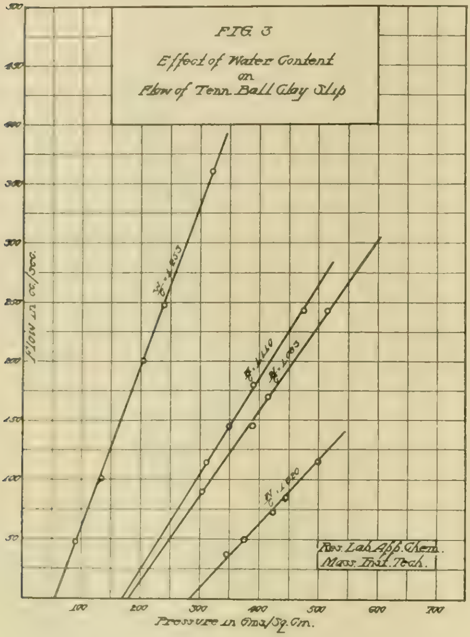
[4] *Trans. Am. Cer. Soc.*, **16** (1914), 392.

[5] Calculated from major and minor axes of tube [illegible]. *Z. physik. Chem.*, **80** (1912), 683.



The clays were prepared for use by grinding until the entire mass passed the 65-mesh sieve. No attempt was made to separate the clay into different fractions. It is known that very fine grinding affects the plasticity, so it was thought best to use a large capillary in the plastometer and avoid grinding the clay so fine that its character would be changed.

All the slips were made by adding weighed amounts of distilled water to a sample of the ground clay as received, but the ratio of water to clay was calculated to a bone-dry basis by making determinations of total water content up to 900° C. on separate small samples of each clay. The losses on ignition thus determined were as follows:

CLAY	Loss on Ignition Per cent
English china	14.20
Georgia kaolin	11.80
Tennessee ball	10.25
English ball	13.00
North Carolina	12.00

SELECTION OF PROPER METHOD OF COMPARING PLASTICITIES

Fig. 3 shows the results obtained with a Tennessee ball clay slip in which the proportion of water was varied. It is evident that as the amount of water is increased there is a continual tendency to increase the mobility and decrease the yield point of the suspension, and that any yield point or any mobility can be obtained with this or any other sample of clay. The property which is a fundamental characteristic of the clay itself, and which cannot be affected by changing the water content, is the functional relationship between these two.

While the term "plasticity" is often loosely used to include a variety of properties, such as lack of excessive shrinkage or cracking on drying, a "soapy" feeling in the slip, as well as a peculiar combination of working properties, there is no question but that the most important physical property in specifying the use of a "plastic" clay is that it shall maintain a reasonably high yield value after enough water has been added to bring its mobility to a point suitable for working. A clay that is much less plastic can be made to have the same yield value by using a very small amount of water, but it would then be too stiff to work; while if its water content were increased to secure the necessary mobility, the yield value would also drop off, resulting in inability to hold its shape after casting.

This brings to the fore the question of the proper basis for measuring and comparing the plasticity of two different clays. One suggestion is the addition of a definite amount of water to the clay, followed by a determination of the flow curve. Fig. 4 shows the results obtained on three different clays with a constant ratio of water to clay of 1.253.[7] It is impossible, however, from an inspection of such results, to decide which is the most plastic clay, because the question immediately arises—if less water had been added to the Tennessee ball clay, thus moving the line to the right, how would its slope compare with that of the other two?

It is therefore apparent that constant water content tests, though quite frequently employed in comparing clays, do not afford a suitable basis for comparison. Instead, the amount[8] of water required to give suitable working properties to the clay is in itself an important property of the clay, which should certainly be determined, but which is distinct

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[6] They were obtained from B. F. Drakenfeld Co. of New York City as representative samples of commercial clays.

[7] All the figures in this paper are plotted in terms of the actual flow (cc./sec.) and pressure (g./sq. cm.) used with the specified capillary. It would be desirable to express these in terms independent of the particular capillary employed, but in view of the previously mentioned uncertainty as to the precise validity of Bingham's simple equations, this has not been done. However, for purposes of comparing results between capillaries that do not vary widely in dimensions, use can well be made of the formula: (see Bingham, "Fluidity and Plasticity," McGraw-Hill, **1922**, p. 233.)

$$\mu = \frac{1.273\, v}{R^3(F-f)}$$

where μ = mobility

f = friction or yield value

v = volume of flow in cc./sec.

F = shearing force applied at the wall of the capillary in dynes/sq. cm.

$$= \frac{980.6\, RP}{2\, L}, \quad \text{where}$$

R = radius of the capillary in cm.

P = applied pressure in g./sq. cm.

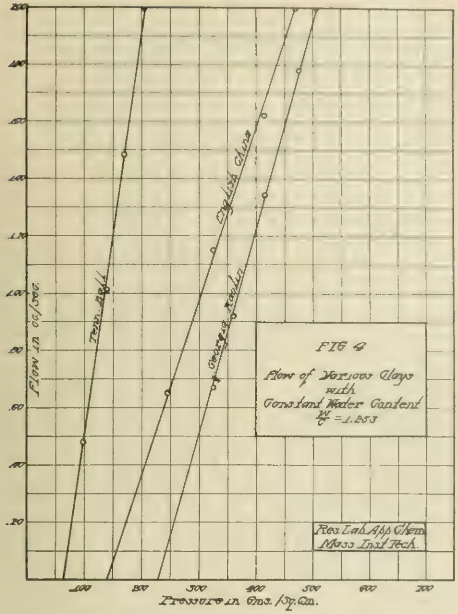
L = length of the capillary in cm.

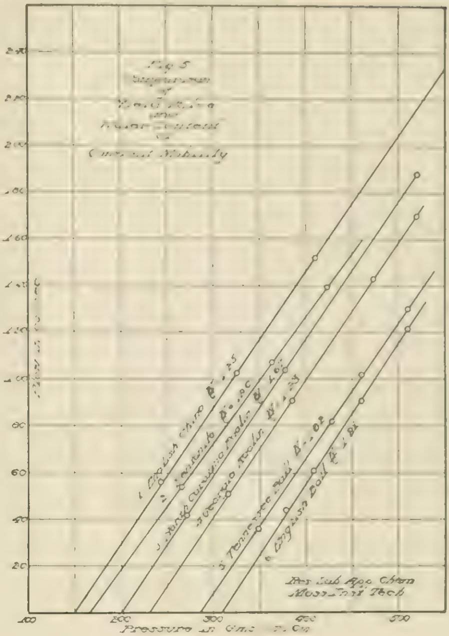
The *calculated* yield values for the capillary used in the foregoing work in terms of *shearing force* in *dynes per sq. cm.* may therefore be obtained by multiplying the graphically determined yield values given in this paper by

$$\frac{980.6 \times 0.06815}{2 \times 5.021} = 6.65$$

and the mobilities by substituting in the above equation.

[8] In the molding range this quantity is sometimes designated by the ceramists as the "water of plasticity."





from plasticity. It is probably related to the amount of shrinkage on drying.

The question next arises as to how to determine when enough water has been added to give the resulting slip-working properties suitable for a given purpose. Several clays of quite different plasticities were made up to possess as nearly as possible similar working properties, and from this test—which should be further confirmed by investigators more closely familiar with ceramic practice—it appears that clays of *constant mobility* possess substantially identical working properties. The correct mobility value naturally varies with the purpose for which the clay slip is used, that selected for these tests being considered approximately correct for casting purposes before "freeing out" with alkali.

Clays should therefore be compared on the basis of (*a*) the amount of water required to give a specified mobility, and (*b*) the magnitude of the yield value when this amount of water has been added, this value presumably being higher the more "plastic" the clay. The testing of clays by this method unfortunately necessitates working by trial and error, and determining two points on the flow curve for each change in the amount of water added, but once the worker is fairly familiar with it he can approximate the proper mobility quite closely by estimation.

It is, of course, conceivable that by studying a large number of clays to which different amounts of water had been added, a definite functional relationship between mobility and yield value would be found to hold for a given type of clay, regardless of the water content, in which case only one measurement would have to be made. For example, it has been found as a rough approximation that for two samples of clay over a twofold range of mobilities the yield value × mobility$^{1.7}$ = a constant, but tests on a third kind of clay did not bear this out.

While the foregoing method of defining and measuring the more important physical properties included under the vague term "plasticity" has thus far been applied only to the casting range, there seems to be no fundamental reason why it should not be extended to the molding range, although the high pressures required and the maintenance of steady flow may present rather serious experimental difficulties.

It should be noted that this method of analyzing "plasticity" into its more important components crystallizes the whole problem and avoids such inconsistencies as the statement of some ceramists that clay passes through a narrow region of "maximum plasticity" in the molding range as the water content is increased. It is certainly highly improbable that any physical property really passes through a maximum with increasing water content, and the popular conception is again believed to be due to the attempt to include too many properties in a single term. In other words, the region of "maximum plasticity" is in reality simply the region of the most desirable working properties (for molding) between the point where the clay is too stiff on account of insufficient water and too sticky or fluid from too much water.[9]

On account of the loose use of the term "plasticity," which can probably never be eradicated, the writers are inclined to recommend that, instead of considering the yield value at constant mobility as a direct measure of "plasticity," the term be dropped entirely when referring to the physical properties of the slips. If water content and yield value at constant mobility should not be found to comprise all the important properties now included under "plasticity," an additional quantitative measurement and term could be added, but the separate properties of the clay should be accurately measured and uniquely defined rather than using a vague general term which means essentially "good working properties" for certain purposes. The situation is analogous to the change from saying that an oil possesses "good lubricating characteristics" to specifying precisely its flash point, cold test, viscosity at different temperatures, etc.

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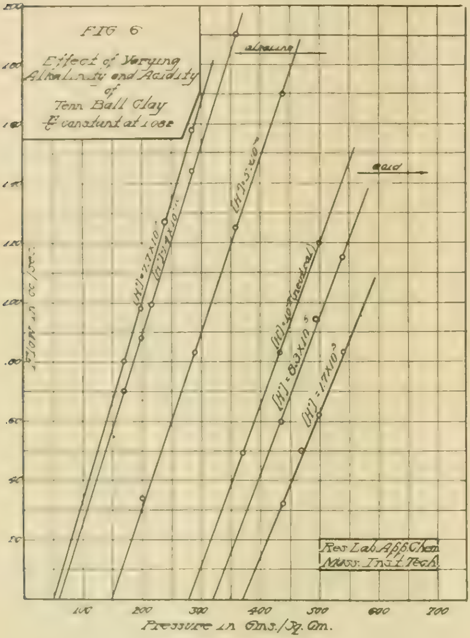
[9] A very recent paper on "The Plasticity of Clays" by J. W. Mellor (Communication from the Clay and Pottery Laboratory, Stoke-on-Trent, No. 53), has thrown interesting light on this question from a somewhat different point of view.



Comparison of Yield Values and Water Contents at Constant Mobility

For the reasons previously discussed, the water content of six samples of clay was adjusted to give a constant mobility suitable for casting, and the yield points and water contents at these mobilities were compared. The results are shown graphically in Fig. 5.

Neglecting for the moment the sample of Bentonite, it will be noted that the order in which the clays arrange themselves with increasing yield value is as follows: English china clay, North Carolina kaolin, Georgia kaolin, Tennessee ball clay, and English ball clay. This corresponds very well with the customary belief as to the relative plasticity of these clays, and thereby confirms the essential validity of the test. It will be noted that the ratio of water to clay required to give these mobilities is quite variable, being as low as 1.02 for the Tennessee ball clay and as high as 1.67 for the North Carolina kaolin. Of the samples tested, the kaolins on the average required more water than the ball clays. The futility of comparing different clays at constant water content is obvious.

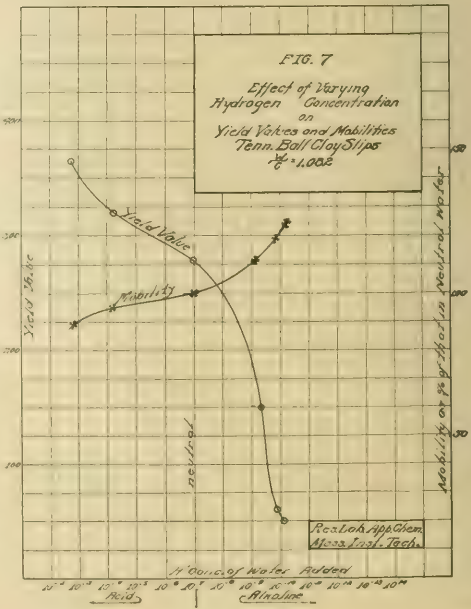
One very interesting sample is the Bentonite, a peculiar soapy clay of which there are large deposits in Wyoming.[10] Although the Bentonite is customarily spoken of as being extremely plastic, it will be noted that on the selected basis of comparison its yield point is rather low, but that the ratio of water to clay required to give the desired mobility is many times as high as for any of the standard clays. It is probable that the common statements with regard to its plasticity are again based on a confusion of ideas resulting from the tendency to make plasticity cover too wide a range of properties. It is, of course, possible that when added in small amounts the remarkable properties of the Bentonite might make a lean slip much more plastic, by coating the larger particles or filling in the voids to give a closer packing effect such as that sought in concrete.

Effect on Yield Value and Mobility of Variations in Acidity and Alkalinity

Having pointed out the two essential physical properties involved in plasticity, it is interesting to study the various methods used to modify the working properties of clays, and to determine just how they influence the fundamental variables of yield value and mobility.

For example, it has long been recognized that the acidity or the alkalinity of the water makes a marked difference in the working properties of the clays. Experiments were therefore carried out with Tennessee ball clay slips, of constant water content but of widely varying hydroxyl or hydrogen-ion concentration, obtained by adding sodium hydroxide or hydrochloric acid to the water. The hydrogen-ion contents are calculated from the amounts added to the water and not measured in the clay slips themselves.

The results shown in Fig. 6 bring out the surprising fact that very wide variations in the hydrogen-ion concentration have a negligible effect on the mobility, but gradually vary the yield value from 50 in alkaline solutions up to 370 in acid solutions. The function of alkalies in "freeing out" the clay, and of acids in "setting up" the clay, thus becomes quite apparent. It is also worthy of note that the yield value of at least this sample of clay can be varied by moderate additions of acids or alkali to cover a wider range than the whole



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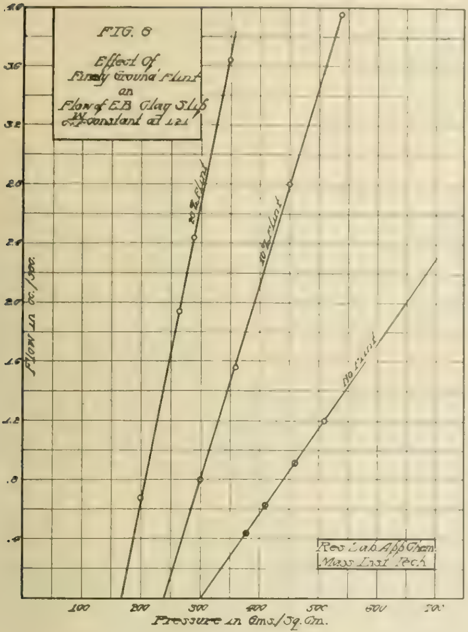
[10] The tests on the Bentonite were made later by Mr. C. E. Ronneberg of this laboratory with a capillary differing slightly in dimensions, but the results were corrected to make them comparable.



series of commercial clays when mixed with distilled water. The necessity, and indeed the potential value, of controlling the hydrogen-ion concentration of clay slips therefore becomes obvious.

Fig. 7 shows graphically how the observed yield value and mobility vary with the H-ion concentration; the sharpest change in the yield value is obviously between a calculated pH of 8 and 10.

Effects of Additions of Nonplastic Materials

Fig. 8 shows the effect of adding varying amounts of finely ground sand (Potters flint) to the clay slip, keeping constant, however, the ratio of water to total dry solids. The flint obviously does not hold nearly as much water as the clay, and the effect of replacing clay with flint is therefore similar to that of adding water to the slip, increasing the mobility and decreasing the yield values. It seems, however, in comparing the results with the addition of water alone, that the effect of the flint on yield value is less than that on the mobility. Additional tests should be made on mixtures of constant mobility and constant ratio of water to clay, but of variable amount of flint.

The foregoing study is obviously preliminary in nature, but it is being continued by the junior author at the Bureau of Standards, a thorough investigation of the whole problem being under way.

Acknowledgment

The writers desire to acknowledge the helpful suggestions of Professor Bingham in connection with the inauguration of the work and the preparation of the paper.

Moving Picture Films

In line with the effort of THIS JOURNAL to supply its readers with information in regard to available moving picture films of industrial and educational value, the following list has been compiled. Data in regard to the source of these films may be obtained from the editorial office.

Acetylene Flame
Aids to Cupid (Perfumes)
Air
Air Nitrate
American Rocquefort Cheese. Made from Cow's Milk
Analysis of Motion
Aqua
Asbestos for a Thousand Years
Asphalt Industry
Asphyxiating Gases
Automobile Starting and Lighting

Babcock-Henry Milk Test
Belt Making and Tanning
Bleaching

Cane Sugar
Cane-Sugar Industry of the United States
Cane-Sugar Refining
Carbonic Gas
Casinghead Gas and Pipe Lines
Casting Milk Bottles
Catching and Canning Oregon Salmon
Cement and Concrete Tests
Chemical Action
Chemistry
Chemistry of Combustion
Chocolate and Cocoa Industry
Chu Chu
Cigars for Kings and Millionaires
Coal Mining in France
Cocoa
Cocoa and Chocolate from Bean to Cup
Cocoa Industry in Trinidad
Coconuts and Copra
Colombia Sugar Plantation
Concrete Industry
Conductivity of Heat
Copra
Copper Mining, Milling and Smelting
Copper Smelting
Cotton Manufacture
Crystals, Their Making, Habits, and Beauty
Crystallization
Cultivating Rubber Plants and Making Rubber Shoes
Cultivation of Rubber

Decomposition of Ultra-Rapid Movements
Delcolight
"De-Light"
Demonstration of Inflammability of Coal Dust and Use of Rescue Apparatus
Dust Explosions in Mills and Elevators
Dust Explosions in Threshing Machines
Dynamite-Making

Earth and Moon
Earth and the Worlds Beyond
Electrical Precipitator
Electrolysis of Metals
Experiments with Liquid Air
Experiments with Sulfur
Expert Glassblowing
Explosive Dusts

Famous Experiments in Electricity and Magnetism
Felt
Fire Prevention
Flaming Ice
Formation of Dew
From Blast Furnace to Finished "National" Pipe
From Flax to Linen
From Mine to Molder
From Pig Iron to Finished Products
From Pulp to Paper
From Rubber Tree to Fountain Pen
From Trap to Can
From Wheatfield to Oven
From Wheat to Flour
Frontiers of a Forbidden Land

Getting Acquainted with Bacteria
Glimpses of Making Bricks, Concrete Blocks, and Steel Rails
Goodbye, Boll Weevil!
Grape Juice Industry
Gypsum

Hang It All (Wall Paper)
Heat
How a Blossom Opens
How Charcoal Is Made
How Life Begins
How Movies Move
How Petroleum Is Produced
How Plaster Is Obtained
How the Telephone Talks
Hydrogen

Just Kids (Gloves)

Kelp Industry

Lead Industry
Light
Liquid Air
Liquid Air and Applications of Intense Cold
Lubrication

Made Game
Magic Clay
Making a Silk Hat
Making Brushes
Making Chocolate
Making Condensed Milk
Making Maple Sugar
Making Natural Color Films
Making of Fine Tools
Making of Pure Foods in Battle Creek
Making of Soap
Making of White Lead
Making Rubber Tires
Making Russian Caviar
Manufacture and Use of Sulfate of Ammonia
Manufacture of Adhesives
Manufacture of Breakfast Food
Manufacture of Charcoal
Manufacture of Coke
Manufacture of Face Brick
Manufacture of Glue
Manufacture of Matches
Manufacture of Steel for Sheets and Plates
Manufacture of Varnish
Manufacture of Zinc Oxide
Manufacturing Paper Money
Marvels of Crystallization
Match-Making
Meat-Packing
Mechanics of Fluids
Mechanics of Fluids in Motion
Mechanics of Solids
Microscopical View of the Blood Circulation
Mining and Extraction of Radium from Carnotite Ore
Modern Metallurgy
Modern Oil-Refining Plant
Modern Sugar Refining
Molecular Mechanics
Muscle Shoals Nitrate Plant
Mysteries of Snow

One of the World's Great Copper Mines
Origin of Coal
Oxygen

Paint and Varnish Making
Physics Made Amusing
Pickling Some of the "57"
Picturesque in American Science
Picture Story of Tea and Coffee
Pictures in Chemistry
Production and Use of Asphalt
Pure Foods—Oleomargarine

Rainey's African Hunt
Romance of a Window
Romance of Gloversville
Rope Industry
Rough Stuff (Carborundum)
Safety Lessons in a Metallurgical Plant
Salt Industry
Science of a Soap Bubble
Scientific Amusements

Purifying Sodium Hydrosulfite: A Modification of Jellinek's Method[1,2]

By Walter G. Christiansen and Arthur J. Norton

Department of Pharmacology, Harvard Medical School, Boston, Mass.

In the following paper an apparatus that has given satisfactory results in purifying sodium hydrosulfite is described, and some changes are made in Jellinek's procedure. One of the features of the apparatus, a combined filtering and stirring device, might be useful in processes other than this. Stable 98.3 per cent pure hydrosulfite is obtained in 42 per cent yields.

The ferricyanide method has been found to be superior to either the copper or silver method for the analysis of hydrosulfite.

As THE toxicity and sulfur content of arsphenamine prepared by reduction of 3-nitro-4-hydroxyphenyl-arsonic acid with commercial sodium hydrosulfite can be made to vary between wide limits, depending upon the conditions under which the nitro group is reduced,[3] and as commercial hydrosulfite usually is of 80 to 87 per cent purity, it became important to determine whether the hydrosulfite itself or the impurities present in commercial samples cause the variations which are obtainable. For this purpose, it was necessary to secure hydrosulfite in a pure form. Jellinek[4] developed a method of purifying commercial hydrosulfite which gave, in a 50 per cent yield, material analyzing 99.4 per cent $Na_2S_2O_4$; this is the average of a number of experiments. While using Jellinek's method it has been found possible to modify his apparatus and procedure in many ways so that a simpler and more rapid process has been evolved by which pure sodium hydrosulfite may be obtained. After the apparatus has been assembled, it is possible to obtain in $4\frac{1}{2}$ hrs. a 42 per cent yield of hydrosulfite 98.3 per cent pure from commercial material of approximately 85 per cent purity. In outline, the procedure is to saturate an aqueous solution of hydrosulfite with sodium chloride, thereby precipitating $Na_2S_2O_4.2H_2O$, which must be dehydrated and dried in order to be stable; all the manipulating must be done *in vacuo* or in an atmosphere of carbon dioxide.

Apparatus

Carbon dioxide is obtained by running hydrochloric acid (1:2) from an elevated bottle through an intermediate bottle, which serves as a reservoir for CO_2 developed in excess of the amount leaving the generator, onto marble contained in a liter suction flask; this flask, M, carries a siphon to remove spent acid. The gas is washed twice with 10 per cent aqueous sodium bicarbonate and once with water. At this point, a shunt containing a calcium chloride tube is inserted so that dry carbon dioxide can be used after the hydrosulfite has been dried. A T-tube with one arm dipping into a tube of mercury serves as a safety valve.

A is a 600-cc. bottle, the bottom of which has been replaced by a piece of canvas with hardened filter paper on each side; the bottle is firmly cemented into a Büchner funnel with litharge and glycerol. The rubber stopper in A has 3 holes—one for a tube to admit carbon dioxide, another for a tube containing a stopcock, 1, and leading to the bottom of bottle B (750 cc.), and the third for a $\frac{1}{2}$-in. glass tube closed by a rubber stopper; all three tubes extend only slightly below the stopper.

B is closed with a rubber stopper through which 4 glass tubes are inserted. One tube, containing a stopcock, 2, connects with the bottom of the Büchner funnel and extends just below the stopper. Another tube, also containing a stopcock, 3, and dipping just below the stopper, is connected to a water pump which has a mercury manometer attached to it. Of the two remaining tubes, both of which pass to the bottom of B, one is the tube mentioned above connecting with A; the other ($\frac{1}{4}$-in. inside diameter) is joined by a short rubber tube and pinch clamp, 4, to a glass tube extending just below the stopper of bottle C (1 liter).

C, resting on several steam bath rings in a 2-liter beaker, has a 5-hole rubber stopper; one hole is in the center and the others are near the edge. Through one of the outer holes passes the tube connecting with B. Two of the holes are fitted with right-angle tubes extending just below the stopper; one is to admit carbon dioxide, the other, containing a 3-way cock, 5, leads to a 2-liter suction flask and thence to the water pump. The remaining outer hole has a short $\frac{1}{2}$-in. tube closed by a solid rubber stopper. The carbon dioxide tubes of bottles A and C are connected to a 3-way cock, 6. Through the center hole of C there is a short heavy-walled piece of hard rubber tube which extends a little below the stopper and about $\frac{1}{2}$ in. above it; this rubber tube serves as a sleeve for a combined filtering and stirring device.

The filtering and stirring device is constructed by sealing a glass funnel to a long piece of glass tube to which 2 short closed tubes have been sealed on opposite sides about 2 in. above the conical part of the funnel. To the ends of these tubes are attached vertical glass rods, the lower ends of which are flattened and bent so as to act as scoops. These scoops are level with the lower end of the funnel and slightly away from it. The funnel is closed with a Hirsch plate over which a piece of canvas is tightly sewed. A small hole is blown in the upper part of the long glass tube and then the upper end of this tube is sealed off. This device is passed through the hard rubber sleeve, and a snugly fitting glass T-tube, *d*, is slipped onto the upper end of the glass tube and firmly fixed by wiring on rubber tubes so that the side arm is opposite the hole in the long glass tube. The side arm is, or may be, connected to the remaining arm of cock 5. The closed end of the filter-stirrer is joined by a rubber stopper to a pulley which connects with a motor. Over the top of the hard rubber sleeve is a tightly fitting rubber tube which fits the filter-stirrer loosely but which can be made tight by wiring. When stirring is in progress this rubber tube is allowed to be loose around the filter-stirrer and the side arm is disconnected at *e* from the 3-way cock and closed by a glass plug. At all other times the rubber tube is wired tightly and the side arm is connected to the 3-way cock.

Procedure

All solutions, except the one of caustic soda and absolute alcohol which are used in the dehydration and drying, are

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[1] Received June 15, 1922.

[2] This is the eighth of a series of studies on the properties contributing to the toxicity of arsphenamine being made under a grant from the United States Interdepartmental Social Hygiene Board to the Harvard Medical School. The work is under the general direction of Dr. Reid Hunt.

[3] Christiansen, *J. Am. Chem. Soc.*, **43** (1921), 2202; **44** (1922), 847.

[4] *Z. anorg. Chem.*, **70** (1911), 93.

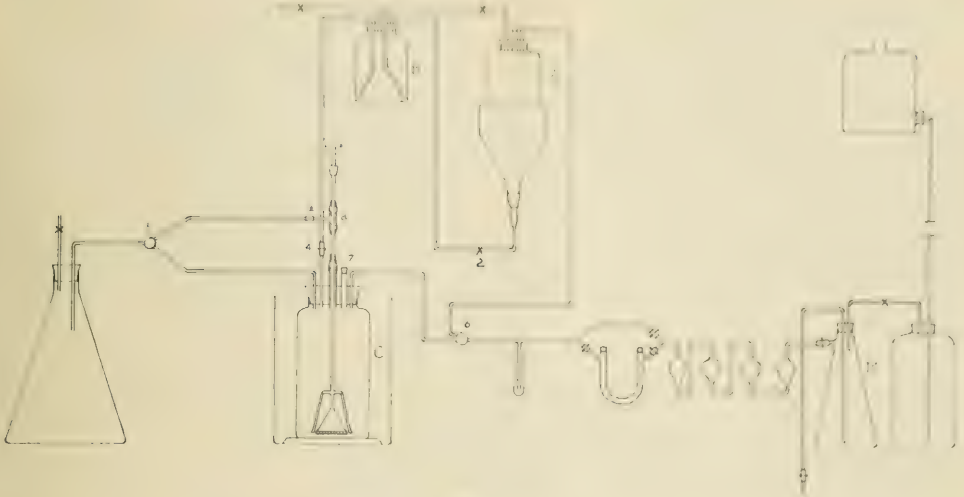

FIG. 1

saturated with washed carbon dioxide, and all pieces of rubber are boiled with alkali and then with water before use. After the apparatus is assembled and made perfectly tight, it is evacuated and filled several times with carbon dioxide; 165 g. of finely ground C. P. sodium chloride are introduced into C through 7, and C is again evacuated and filled with carbon dioxide. To 600 cc. of freshly distilled water, cooled in an Erlenmeyer flask in presence of carbon dioxide, 150 g. commercial hydrosulfite are added, with mechanical stirring to prevent caking. Several grams of Superfiltchar,[5] which has been kept *in vacuo* over caustic soda and pyrogallol for several days, are added to adsorb any fine material which might pass through the filter. With all the stopcocks closed and with carbon dioxide passing into A, the solution is quietly poured into A, and, after opening 2 and 3, is filtered into B. A perfectly clear, sparkling, yellow filtrate is obtained; the apparatus has been so made that in event of turbidity the filtrate can be blown back into A through 1 by passing carbon dioxide through C into B; but to date this has never been necessary. With only 1 and 4 open and the stirrer in motion, the solution is forced by carbon dioxide from B onto the salt which precipitates $Na_2S_2O_4.2H_2O$; the agitation is continued for 30 min.

In the washing, dehydrating, and drying of the precipitate, Jellinek's method[6] is adhered to with a few changes in technic. As a result of the construction of C it is possible to efficiently agitate during the salting out, washing, and dehydration of the hydrosulfite and to remove the liquor by filtration without disturbing the apparatus. The material is heated during dehydration and drying by filling the beaker with warm water and passing in steam to obtain any desired temperature. The first washing is made with salt solution just under saturation so that any undissolved salt will be removed. The wash solutions are introduced through 7, using a wash bottle the tip of which has holes on the sides instead of the end so that the solution can be blown against the walls of C, thereby washing the solid down. Formation of a coarse product—Jellinek[6] indicated the importance of this property in increasing the stability of the material—is favored during the dehydration by vigorous agitation, rapid heating to 60° C., and maintenance of this temperature.

It has been found advantageous to filter to a slightly smaller bulk before dehydrating than Jellinek indicated, so that the walls of C can be rinsed with a little salt solution at the beginning and near the end of the dehydration. After the product has been dried, C is filled with dry carbon dioxide because hydrosulfite rapidly undergoes decomposition in the presence of moisture. In nine consecutive experiments 42 per cent yields of coarse white stable sodium hydrosulfite averaging 98.3 per cent (97.7 to 98.9) pure have been obtained.

In some preliminary experiments the white, hydrated solid underwent extensive decomposition and turned black during the dehydration. This was found to be caused by small amounts of iron in the supposedly C. P. caustic soda added just before the material was heated, the black color resulting from ferrous sulfide. Subsequently, the alkali was made from sodium and distilled water. Similar decompositions took place to a very slight extent when some salt containing traces of iron was used. At another time an attempt was made to use small amounts of litharge-glycerol cement in modifying C. Although only a minute amount of lead was exposed to the vapors in C, enough of it was removed to cause slight darkening of the liquor during dehydration. Evidently great care must be exercised to exclude heavy metals.

ANALYSIS

A satisfactory method of analysis for the purified product was not easily secured; the copper method[7] gave low results, and the silver method[8] gave high results. By adding the solid hydrosulfite from a weighing bottle with a small spatula to a stirred solution of a known amount, about 1 g. of C. P. potassium ferricyanide in 50 cc. water containing a little nonacidified ferrous ammonium sulfate solution till the blue color disappears, satisfactory analyses checking to 2 parts per 1000 were obtained.[9] The reaction takes place according to the following equation:

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[5] A high grade of decolorizing carbon.

[6] *Z. anorg. Chem.*, **70** (1911), 113.

[7] Helwig, *Am. Dyestuff Rep.*, **7** (1920), 12.

[8] Smith, *J. Am. Chem. Soc.*, **43** (1921), 1307.

$$2K_3Fe(CN)_6 + Na_2S_2O_4 + 2H_2O = 2K_3NaFe(CN)_6 + 2H_2SO_3$$

As this method of analysis gives results that are a few tenths of a per cent low, the products obtained in this work are nearly 99 per cent pure. A number of purified samples gave positive tests for small amounts of chloride. A sample was oxidized in alkaline solution with C. P. sodium peroxide, and sulfate equivalent to 36.69 per cent sulfur in the hydrosulfite was found as against a calculated value of 36.78.

In determining the stability of the product a fresh sample analyzing 98.9 per cent pure was shaken at frequent intervals in a bottle with an excess of air for 3 hrs. and was then exposed in a thin layer to the air for 16 hrs. The temperature was 82° to 87° F. and the humidity was fairly high at the time of this experiment. Even under these conditions the purity dropped only slightly (1.3 per cent). Another sample of the same lot was ground in a mortar and then subjected to the foregoing treatment; in this case the purity dropped 19 per cent. These figures bring out the relation between the coarseness and the stability of the material very effectively.

ACKNOWLEDGMENT

The writers wish to acknowledge their indebtedness to Dr. Reid Hunt for his interest in the work and to Mr. Henry W. George for his invaluable assistance in constructing the apparatus.

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[9] After we had been using this method for some time, we found that G. Bruhns, *J. Chem. Soc.* (*London*), **118A** (1920), II, 395, had used a similar one.

Effect of Hydrogen-Ion Concentration upon the Analysis of Vegetable Tanning Materials[1]

By John Arthur Wilson and Erwin J. Kern

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At a meeting of the Society of Leather Trades' Chemists in London, September 8, 1921, an international commission was appointed, under the chairmanship of H. R. Procter, to consider suggested revisions of the official method of tannin analysis. Among the things which the commission was called upon to investigate was the effect of change of pH value, the importance of which had previously been pointed out by Procter.[2] Later Thompson, Seshachalam, and Hassan[3] made a preliminary study of the effect of adding acetic and hydrochloric acids to extracts of quebracho, mimosa, mangrove, gambier, myrobalans, chestnut and oak wood, and found that the addition of small amounts of acid affected nearly all the determinations made. The present investigation represents an attempt to deal with the subject somewhat more systematically, and was confined to a study of the behavior of quebracho extract at different pH values.

AMERICAN LEATHER CHEMISTS ASSOCIATION METHOD

A SERIES of solutions of solid quebracho extract was prepared according to the official method of the American Leather Chemists Association,[4] except for the addition of hydrochloric acid or sodium hydroxide to produce approximately the desired pH value before making each solution up to the required volume. The pH values were finally determined at 20° C. by means of the hydrogen electrode, and the solutions were analyzed according to the official method. The results, which are shown in Table I and Fig. 1, were calculated on the basis of the original extract, no allowance being made for the added acid or alkali, so that the percentages recorded for nontannin are higher than they should be, but this was done so as to record the more significant values for tannin and insolubles on the basis of the original extract.

In order to show the effect of valency, we ran a second series of determinations, like the first except for the fact that sulfuric acid and lime were used to alter the pH values. The results of these are shown in Table II and Fig. 2.

The solution receiving no addition of acid or alkali had a pH value of 4.60. As the pH value was lowered from this by the addition of either sulfuric or hydrochloric acid, there was an increase in the percentage of insoluble matter found and a corresponding decrease in percentage of tannin found. Sulfuric acid proved slightly more effective than hydrochloric in increasing the percentage of insoluble matter. With increasing pH value, there was first a decrease in the amount of insoluble matter, and the unfiltered solution gradually became more nearly transparent. In the case of NaOH this continued without a break, but with $Ca(OH)_2$ an abrupt change occurred at the neutral point, and with further rise of pH value the tannin was precipitated in increasing amounts. The curve for insoluble matter in Fig. 2 furnishes an interesting proof of the accuracy of Procter's limewater method[5] for determining the percentage of acid in tan liquors.

Since tanning extracts often undergo fermentation during shipment, or upon storing, with a corresponding increase in hydrogen-ion concentration, it is not surprising that analysts sampling a shipment at different times fail to obtain concordant results by the A. L. C. A. method. Since the chief aim of this method is the ability of different analysts to get concordant results, the method would serve its purpose

TABLE I—EFFECT OF HCl OR NaOH UPON THE ANALYSIS OF QUEBRACHO EXTRACT BY THE A. L. C. A. METHOD

	pH Value	Insoluble Per cent	Nontannin Per cent	Tannin Per cent
HCl	1.86	14.72	6.70	61.63
	2.59	12.76	6.63	63.24
	3.60	10.71	6.58	65.09
	3.85	10.06	6.62	65.70
	4.60	8.80	6.62	66.95
NaOH	5.60	5.67	6.92	69.96
	5.88	4.15	7.55	71.05
	6.56	3.65	8.00	71.63
	7.29	3.52	8.21	72.15
	7.34	3.50	8.13	72.07
	7.97	2.55	8.78	72.65
	8.07	2.70	8.58	72.60
	8.89	1.58	17.70	67.80
	9.41	0.98	32.42	58.53
	11.35	0.35	70.55	30.35

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[1] Presented before the Division of Leather Chemistry at the 64th Meeting of the American Chemical Society, Pittsburgh, Pa., September 4 to 8, 1922.

[2] *J. Soc. Leather Trades' Chem.*, **5** (1921), 219.

[3] *Ibid.*, **5** (1921), 389.

[4] *J. Am. Leather Chem. Assoc.*, **16** (1921), 113.

[5] "Leather Industries Laboratory Book," Spon, London, **1908.**

more efficiently by requiring that the analysis be made on a solution of definite pH value.

RATE OF FILTRATION

Thompson and his coworkers found that the rate of filtration of tan liquors was increased by the addition of acid. While filtering, for the determination of insoluble matter, the various solutions mentioned in this paper, we kept a record of the time required to collect 100 cc. of filtrate, after the paper had been tanned for exactly 1 hr. In order to show the change as accurately as possible, we selected filter paper of uniform thickness and repeated each measurement several times. The resulting values are plotted in Fig. 3. It will be of general interest to note that the untreated liquor was one of the most difficult to filter.

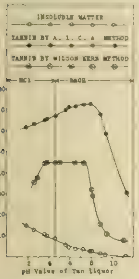

FIG. 1

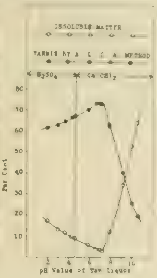

FIG. 2

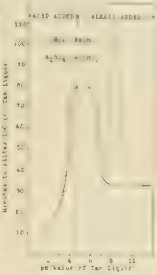

FIG. 3

FIG. 1—SHOWING HOW THE ADDITION OF HYDROCHLORIC ACID OR SODIUM HYDROXIDE AFFECTS THE ANALYSIS OF QUEBRACHO EXTRACT

FIG. 2—SHOWING HOW THE ADDITION OF SULFURIC ACID OR CALCIUM HYDROXIDE AFFECTS THE ANALYSIS OF QUEBRACHO EXTRACT

FIG. 3—SHOWING HOW THE RATE OF FILTRATION OF A SOLUTION OF QUEBRACHO EXTRACT IS ALTERED BY THE ADDITION OF ACIDS AND ALKALIES

The differences in rate of filtration may be ascribed largely to differences in the degree of dispersion of some of the solid matter, which we followed by means of the Tyndall cone. A very fine or very coarse dispersion filtered much more quickly than one of intermediate degree. The effect was very marked in the solutions to which lime was added. With the first appearance of turbidity, after a pH value of 7 was passed, there was a tremendous increase in time required to filter 100 cc., but as the precipitate grew coarser the liquor filtered much more quickly.

WILSON-KERN METHOD

In earlier papers[6] the authors have shown that the A. L. C. A. method gives values for tannin that are much too high, because of the inclusion of a variable fraction of nontannin that can easily be separated from the hide powder by washing. They proposed a new method for determining the true tanning value of tanning materials that is receiving some attention from the present international commission. In studying the effect of change of pH value upon this method, we prepared a series of liquors from the sample of solid quebracho extract as described in the paper, "The Determination of Tannin,"[7] except for the addition of HCl or NaOH to give the desired pH values. The results of a series of determinations are given in Table III, and the values for tannin are plotted in Fig. 1 for comparison with those obtained by the A. L. C. A. method.

TABLE II—EFFECT OF H_2SO_4 OR $Ca(OH)_2$ UPON THE ANALYSIS OF QUEBRACHO EXTRACT BY THE A. L. C. A. METHOD

	pH Value	Insoluble Per cent	Nontannin Per cent	Tannin Per cent
H_2SO_4	1.95	17.10	7.97	[illegible]
	2.97	[illegible]	[illegible]	[illegible]
	3.66	[illegible]	[illegible]	[illegible]
	4.27	[illegible]	[illegible]	66.32
	4.60	[illegible]	6.62	[illegible]
$Ca(OH)_2$	[illegible]	[illegible]	6.63	[illegible]
	6.63	3.42	6.13	73.02
	[illegible]	[illegible]	6.80	[illegible]
	[illegible]	2.70	7.03	72.90
	[illegible]	[illegible]	9.58	[illegible]
	[illegible]	11.93	8.45	[illegible]
	[illegible]	34.50	[illegible]	40.28
	[illegible]	[illegible]	17.17	25.61
	[illegible]	63.84	19.98	[illegible]

A practically constant value for tannin is obtained over the wide range of pH values 3.6 to 7.3. Where the falling off in percentage of tannin occurs at pH values higher than 7, the results should not be considered as found by this method, because in each case the residual solution gave a test for tannin, by the gelatin-salt test, whereas the method specifies that the determination is to be discarded whenever such a test is obtained. Apparently the hide-tannin compound is unstable, or possibly does not form at all, at pH values higher than 8. The fact that some combination seemed to take place at higher pH values may be apparent only, because the powders, wet with liquor, were washed with distilled water having a pH value of about 5.8. The stability of the hide-tannin compound at different pH values is being studied as a separate work.

The falling off in percentage of tannin found at pH values below 3 may be the result of the great swelling of the hide powder in liquors of low pH value. A complete investigation of this point has not yet been made.

TABLE III—EFFECT OF ADDING HCl OR NaOH UPON THE DETERMINATION OF TANNIN IN QUEBRACHO EXTRACT BY WILSON-KERN METHOD

	pH Value Initial	pH Value Final	Gelatin-Salt Test	Tannin Per cent
HCl	1.86	2.57	Negative	[1]
	2.59	4.20	Negative	35.50
	2.95	4.62	Negative	37.73
	3.60	5.05	Negative	44.35
	3.85	5.35	Negative	44.96
NaOH	4.60	5.57	Negative	44.83
	5.03	5.70	Negative	44.87
	6.52	6.50	Negative	44.68
	7.31	7.00	Positive	44.65
	8.04	..[2]	Positive	31.87
	8.18	.	Positive	29.30
	8.91	.	Positive	15.55
	9.54	..	Positive	10.88
	11.10	9.15	Positive	7.93

[1] Hide powder could not be washed.
[2] Hydrogen electrode became poisoned very quickly.

The pH values of the liquors were determined both before and after the 6-hr. shaking with hide powder. The curve representing tannin is plotted against the initial pH value of the solutions because not all the final pH values could be determined. When alkali is added to a tan liquor so as to produce a pH value of about 9, there is no difficulty in measuring the pH value immediately after the addition, but after a few hours the determination can no longer be made because the liquor then poisons the hydrogen electrode. This change in tan liquors occurring at a pH value of about 9 has been noted before.[8]

CONCLUSION

The percentage of tannin in quebracho extract indicated by the A. L. C. A. method increases with pH value to a maximum at 8, and then decreases rapidly toward zero. On the other hand, pH value appears to have no effect upon the determination of tannin by the Wilson-Kern method over the range 3.6 to 7.3, but the rate of tanning of hide powder decreases rapidly with increasing pH value above 7.

The rate of filtration of tan liquors is markedly affected by change of pH value, which may be attributed to changing degrees of dispersion of some of the solid matter.

The addition of lime to tan liquors causes a precipitation of tannin, but only at pH values above 7.2.

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[6] THIS JOURNAL, 12 (1920), 465, 1149; 13 (1921), 772.

[7] *Ibid.*, 13 (1921), 772.

[8] THIS JOURNAL, 13 (1921), 1025.

The Drainage Error in Measurements of Viscosity by the Capillary Tube Method[1]

By **Eugene C. Bingham** and **Henry L. Young**

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IF THE viscometer already described[2] is used for very viscous materials, there are certain corrections to be considered which are ordinarily not necessary, presuming that a reasonable precision is desired of, say, 0.2 per cent.

A drainage correction arises from the fact that the volume of flow is assumed to be the volume of a certain double cone-shaped bulb which has been calibrated by means of some known liquid. If the unknown liquid does not drain as well as the calibrated liquid, the volume of flow will be too small, and vice versa.

The drainage error may, of course, be decreased to any extent that is desired by simply increasing the time of flow, but it is wasteful to have the time of flow for a single determination consume several hours if an equally good determination can be made in a few minutes by using a more suitable apparatus or previously determined correction terms. Happily, both of these alternatives are open to us. By using the plastometer, no drainage correction is necessary, and with the viscometer simple corrections may be made.

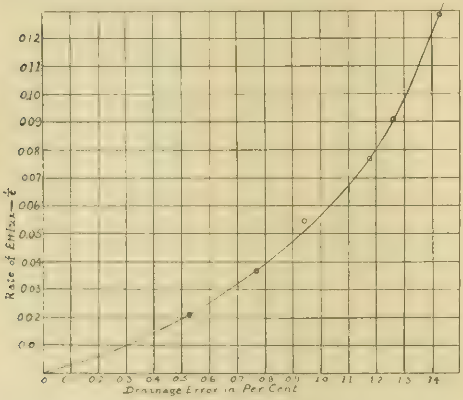

FIG. 1

In our experiment, we have used double cone-shaped bulbs having the following volumes determined by means of mercury—2.50, 3.68, 8.80, 11.46, and 24.42 ml. Liquids of known viscosity were driven under known head through a capillary attached to the lower end of the bulb. The volume of the bulb being known and the volume of efflux found by direct weighing, the drainage error was determined by difference. As an example we give the values obtained for the 24.42 ml. bulb in Table I and Fig. 1. In the figure the drainage error is plotted against the rate of efflux, which is taken as proportional to the reciprocal of the time in minutes ($1/t$). It is seen that in order to determine the viscosity of castor oil at 20° with an accuracy of 0.2 per cent, it is necessary to make the time of flow about 2 hrs. unless a correction is made for drainage error.

Experiments were made to determine how, with a given time of efflux (15 min.), the drainage error varied with the viscosity of the liquid used. Our experiments indicate that the drainage error may be taken as a linear function of the viscosity. Castor oil, lard oil, linseed oil, and certain mineral oil mixtures were used.

TABLE I—DRAINAGE ERROR FOR A BULB HAVING A CAPACITY OF 24.42 ML., USING CASTOR OIL AT 20°

Time in Min. t	Average Rate of Efflux $1/t$	Drainage Error Per cent
7.80	0.128	1.40
7.84		1.46
9.79	0.102	1.27
9.80	.....	1.36
13.08	0.0765	1.20
13.08	.....	1.15
18.41	0.0544	0.91
18.38	.....	0.97
27.63	0.0363	0.80
27.46	.....	0.74
48.16	0.0209	0.51
47.88	.....	0.55

As a result, we have prepared Table II to show the drainage corrections for liquids of different viscosities and for different times of efflux. In using the table, suppose that a liquid of approximately 750 centipoises was determined in a time of efflux of 30 min. By interpolation of the table, the error due to faulty drainage is found to be 0.5 per cent. In the formula for viscosity,[3] the volume of efflux is 0.5 per cent less than the actual capacity of the bulb; hence we obtain the final simple formula,[4] $\eta = 1.005\, C\, p\, t - C'\, \rho/t$.

If the material used is not a true fluid but partakes of the character of a plastic solid, it is evident that this table of corrections will not apply. Furthermore, a source of difficulty arises in that some liquids do not wet the walls of the bulb uniformly, so that the drainage is uneven.

TABLE II—DRAINAGE CORRECTIONS FOR DIFFERENT VISCOSITIES AND TIMES OF EFFLUX IN PER CENT

	EFFLUX						
Viscosity in Cp.	10 Min.	15 Min.	30 Min.	45 Min.	60 Min.	100 Min.	150 Min.
1000	1.2	1.0	0.7	0.5	0.4	0.3	0.2
500	0.6	0.5	0.3	0.2	0.2	0.1	0.1
100	0.1	0.1	0.1	0.1	0.0	0.0	0.0
1	0.0	0.0	0.0	0.0	0.0	0.0	0.0

Leaving the question of the drainage error, the question may arise as to whether the heat developed within the capillary, due to the work done in overcoming viscous resistance, is sufficient to make an additional correction desirable.

Take as an example one of our experiments with castor oil at 20°, using a pressure of 214 g. per sq. cm. and a volume of efflux of 7 ml. The work done amounts to 1,470,000 ergs, which is equivalent to 0.035 cal. Assuming a specific heat of 0.48, the elevation of the temperature of the oil on leaving the capillary should have been 0.01°, provided that no heat had been conducted out through the material of the capillary. This would affect the viscosity of the castor oil by only 0.08 per cent, which we must regard as negligible at present.

In plastic flow much higher amounts of energy are absorbed, but the accuracy at present is not better than 0.5 per cent. It will evidently be practicable to make a correction for the heat developed as the necessity arises.

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[1] Presented before the Division of Physical and Inorganic Chemistry at the 63rd Meeting of the American Chemical Society, Birmingham, Ala., April 3 to 7, 1922.

[2] Bingham, "Fluidity and Plasticity," **1922**, p. 76.

[3] Bingham, "Fluidity and Plasticity," **1922**, p. 23.

[4] *Ibid.*, p. 74.

The Determination of Gums in Sugar Products[1]

By H. T. Ruff and James R. Withrow

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Sugar boilers and others responsible for the production of refined from raw sugar recognize that different yields and rates of crystallization may be obtained from two raw sugars of similar sucrose, invert sugar and ash content, that have had the same treatment. It is generally conceded that this difference is due to the gums. The gums are presumed to be the strongest molasses formers among the organic nonsugars. This situation is also encountered in the manufacture of raw sugar from the cane.

The problem with which this work is concerned is the selection of a method for determining these gums that could be used for control work or to classify sugar products further than the usual sugar and ash determinations. Our work indicates:

1—Of the various methods proposed for gum determination, the precipitation by ethyl alcohol with hydrochloric acid acidification was found to be the most suitable for a rapid method adapted to control work.

2—The concentration of hydrochloric acid can be varied within rather wide limits without materially affecting the results, but the concentration of the alcohol must be kept within close limits.

3—With suitable precautions, denatured or methyl alcohol can be substituted for the ethyl alcohol.

4—The technic of the method can be simplified, so that its use is not prohibitive for control work.

THE METHODS for determining gum in sugar products may be classified into four groups, according to the precipitant used:

1—Hydrochloric acid-ethyl alcohol methods.[2]
2—Calcium chloride-ethyl alcohol methods.[3]
3—Ferric chloride followed by reprecipitation with alcohol.[4]
4—Lead acetate in alcohol methods.[5]

In addition to these there are methods involving dialysis, but they could not be considered as control methods.

We checked representative methods from each group, using black strap molasses for the tests. Both ethyl and methyl alcohol were used. The following average results were obtained:

	Methyl Alcohol Per cent	Ethyl Alcohol Per cent
HCl-Alcohol (Weichmann)	2.27	2.53
$CaCl_2$-Alcohol (Bellier)	7.38	5.74
Fe_2Cl_6-(Auguet)	0.68	1.00
$Pb(C_2H_3O_2)_2$-Alcohol (Chauvin)	15.9	19.1

In the literature the HCl-alcohol method is generally conceded to give the most reliable results. Some of the methods are proposed only on a basis of their results on solutions of gums in water or pure sugar solution. This may help to account for the large variation that we have found.

For our purpose the $CaCl_2$-alcohol method is objectionable because the precipitation requires 24 hrs. The filtration and washing require more time than the HCl-alcohol method. This is the only case in which the methyl alcohol gives higher results than the ethyl. Possibly $CaCl_2.(CH_3OH)_x$ is formed.

Auguet's Fe_2Cl_6 method from a manipulative viewpoint is the most unsatisfactory of the four. It has these disadvantages: two precipitations and filtrations are involved. The first filtration requires longer than an entire HCl-alcohol gum determination. The gums from the Fe_2Cl_6 precipitation dissolve with difficulty in hot water, and this requires a comparatively large amount of water, which requires as much as three times the alcohol used in an HCl-alcohol precipitation. Compared with the other methods, this method gives abnormally low results.

The $Pb(C_2H_3O_2)_2$-alcohol method has the very obvious disadvantage that it precipitates many other organic nonsugars in addition to the alcohol-insoluble gums, when applied to a product like black strap. This method involves a lead correction and washing with alcohol and ether. It is slower than the HCl-alcohol method.

Requirements of a Method for Gum Determination for Control Work

1—For control work a gum determination should be easily made and should be as rapid as possible

2—The precipitate obtained in the case of a product which has been defecated probably does not represent entirely the true cane gum present in the cane. This precipitate is thus a more or less indirect measure of the gum or substances that retard crystallization, and only comparative results are obtained. In view of this inability to obtain absolute results, almost any method that will give consistent comparative results and is adapted to rapid and convenient manipulation is justifiable.

3—It is our opinion that no method should be used that throws out large amounts of organic nonsugars other than gums. Since the pure cane gum cannot be isolated by any simple procedure, the alcohol concentration should be such that dextrin will be precipitated. Dextrin is also a gum and retards crystallization.

The most suitable method for control work has been shown to be the HCl-alcohol method. This was studied for the purpose of obtaining such alcohol and acid concentrations that slight changes in the concentration would have little effect on the gum precipitate.

Ethyl alcohol is frequently hard to procure, and for this reason substitutes like methyl and denatured alcohol are desirable. Throughout this work we have compared these with ethyl alcohol.

Effect of Sodium Benzoate as Preservative

Five g. of sodium benzoate were added to the stock sirup,[6] using 10-cc. sirup samples. Analysis before and after addition of the preservative showed the following average results:

Before sodium benzoate	After sodium benzoate
0.0296 g. gums	0.0302 g. gums

There is a slight increase in the gum content after adding the sodium benzoate, but this may be an analytical variation.

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[1] Presented before the Division of Sugar Chemistry at the 63rd Meeting of the American Chemical Society, Birmingham, Ala., April 3 to 7, 1922.

[2] L. B. Langguth, Steuerwald, and T. Van der Linden, *Arch. Suikerind.*, **22** (1914), 1033 [*C. A.*, **8** (1914), 3511]; J. J. Hazewinkel, *Ibid.*, **18** (1910), 746 [*C. A.*, **5** (1911), 1850]; *Ibid.*, **19** (1911), 313 [*C. A.*, **5** (1911), 244]; Weichmann, "Sugar Analysis," 3rd ed., p. 134, John Wiley & Sons, Inc., N. Y.; Noel Deerr, "Cane Sugar," **1911**, p. 482.

[3] Bellier, *Ann. fals.*, **3** (1910), 528 [*C. A.*, **5** (1911), 928].

[4] A. Auguet, *Ibid.*, **2** (1909), 136 [*Chem. Zentr.*, **11** (1909), 1011].

[5] A. C. Chauvin, *Mon. sci.*, [5] **1** (1911), 1, 317 [*C. A.*, **5** (1911), 3353]; *Ann. fals.*, **5** (1912), 27 [*C. A.*, **6** (1911), 1074]. X. Rocques and G. Sellier, *Ann. chem. anal.*, **16** (1911), 218 [*C. A.*, **5** (1911), 3635].

[6] Used in all following determinations except as expressly noted otherwise. 1000 g. 96° raw sugar (gums, 0.14 per cent) and 200 g. black strap molasses (gums 2.53 per cent), with water to 2000 cc. This makes a sirup of 47 to 48 per cent solids.

The sirup can be thus kept 4 wks. at ordinary temperatures before any evidences of fermentation appear. Even when bubbles appear there is no perceptible change in the gum content.

EFFECT OF HCl CONCENTRATION ON THE GUM PRECIPITATE

The alcohol concentration was kept constant in these tests while the acid concentration was varied. Ten cc. stock sirup were taken and varying amounts of acid added, but water was added with the acid to make the total added volume 2.5 cc. Then 50 cc. of alcohol (94.5 per cent by volume for the ethyl and 92.7 per cent by weight for the methyl alcohol) were added, and after 30 min. the precipitate was filtered in alundum crucibles, dried 1 hr. at 100° C., weighed, ashed, and reweighed. The gum column in the table represents the net gum content after deducting the ash.

	Ethyl Alcohol			Methyl Alcohol	
Expt. No.	HCl G.	Gums G.	Ash in Gums Pptd. G.	HCl G.	Gums G.
1	0.00	0.1022	0.0472	0.00	0.0987
2	0.02	0 0794	0.0349	0.02	0.0809
3	0.05	0.0364	0.0220	0.05	0.0386
4	0.10	0.0292	0.0213	0.10	0.0283
5	0.15	0.0288	0.0213	0.20	0.0285
6	0.20	0.0288	0.0183	0.30	0.0271
7	0.30	0.0294	0.0105	0.40	0.0264
8	0.40	0.0291	0.0017	0.60	0.0262
9	0.60	0.0279	0.0015	1.00	0.0261
10	1.00	0.0345	0.0014		

These results are shown in Curves I, II, and IV of Fig. 1.

The first portion of the gum curve has a very sharp slope, which breaks off sharply. Calcium salts of the various organic acids can be precipitated by alcohol of this concentration, while the free acids cannot. As soon as sufficient HCl has been added to liberate all these acids, the gum precipitate becomes practically constant. After this point is reached the acid concentration may be varied over quite a range without materially affecting the amount of gums obtained. The concentration recommended by Noel Deerr and by Weichmann falls on the flat portion of this curve. It corresponds to a concentration of about 0.27 g. HCl, as plotted on this curve.

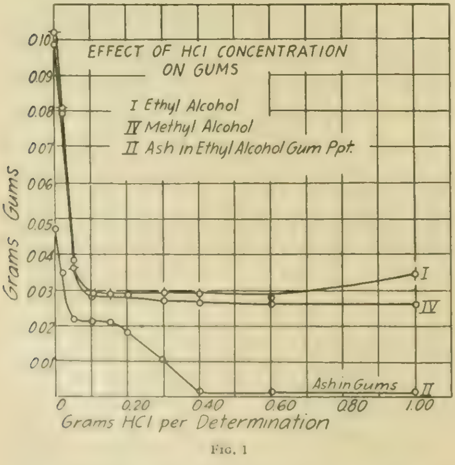

FIG. 1

The combustible matter present in the gum precipitate, and not the ash, determines the amount of gum. It is not necessary to determine this ash to obtain the gums, as is necessary where the filtration is on filter paper. The ash was determined here only as a matter of information.[7]

EFFECT OF VARYING ALCOHOL CONCENTRATION WITH ACIDITY CONSTANT

The acidity used in these experiments is 1 cc. of concentrated HCl per determination for 100 cc. of alcohol. This concentration permits a considerable variation in the acid measurement without affecting the results. This is a convenient concentration and is the same as is recommended by Noel Deerr and by Weichmann. Ten cc. of sirup were used and 0.5 cc. of concentrated HCl added, and then the desired quantity of alcohol in a volume of 50 cc. Filtration was in alundum crucibles for the ethyl alcohol experiments, and in an asbestos mat Gooch for the methyl alcohol experiments. The precipitate was dried 1 hr. at 100° C., weighed, ashed, and reweighed.

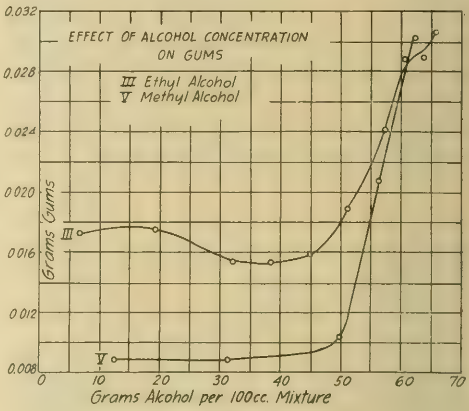

FIG. 2

In the ethyl alcohol runs, Expts. 9 and 10 filtered so slowly that the washing was imperfect. In general, the methyl alcohol precipitates settle faster and filter faster than those of the ethyl alcohol.

Expt. No.	G. Alcohol per 100 Cc. Mixture	Gums	Ash in Gum Pptd.
	ETHYL ALCOHOL		
1	65.4	0.0307	0.0204
2	63.7	0.0290	0.0187
3	60.5	0.0289	0.0156
4	57.3	0.0242	0.0169
5	51.0	0.0190	0.0036
6	44.6	0.0159	0.0022
7	38.2	0.0154	0.0020
8	31.8	0.0154	0.0031
9	19.1	0.0175	0.0023
10	6.4	0.0172	0.0019
	METHYL ALCOHOL		
1	62.2	0.0303	......
2	59.2	0.0262	......
3	56.1	0 0208	......
4	49.6	0.0104	......
5	31.1	0.0089	......
6	12.4	0.0087	......

These data are represented by Curves III and V of Fig. 2.

The higher alcohol concentrations are on a rather steep part of the curves. This abrupt drop in the gums is apparently a dextrin loss. If the alcohol concentrations were carried much higher, there would be danger of throwing out much organic nonsugar and possible sugar. It is evident that the alcohol concentration should be kept within close limits, and as high as the higher concentrations used in these tests.

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[7] The fact that loss on ignition without actual determination of ash is all that is necessary to determine gums is made possible by our use of alundum crucible in place of filter paper commonly recommended. For still more rapid, less precise, work even the loss on ignition might be omitted, if a series of gum determinations were being made on a product with uniform ash character, by taking advantage of the fact, shown on the curves, that above 0.4 g. of HCl per determination, the ash is low and constant. In such a case the ash constancy should be checked occasionally by determining loss on ignition.

COMPARISON OF ETHYL, METHYL, AND DENATURED ALCOHOLS

TESTS ON 94° MOLASSES-HOUSE SUGAR—This sugar was made into a 50 per cent sirup and filtered by suction through asbestos. 20 cc. of sirup, 1 cc. of HCl, and 100 cc. of alcohol were used for each determination.

AVERAGE PERCENTAGE OF GUMS

A	B	C
0.252	0.252	0.247

A—Pure ethyl alcohol, 94 per cent by volume.
B—90 per cent ethyl alcohol and 10 per cent methyl alcohol, 92 per cent by weight.
C—Methyl alcohol (commercial), 92 per cent by weight.

These results indicate that for this sugar these alcohols give results that are practically identical.

Another sample of sugar was checked against completely denatured alcohol and the following average results obtained:

Ethyl Alcohol (94 per cent)	Denatured Alcohol
0.266 per cent gums	0.281 per cent

This alcohol was denatured by the following formula (parts by volume): 100, ethyl alcohol; 2, methyl alcohol; 0.25, pyridin; and 0.50, benzine. This denatured alcohol showed 94 per cent by volume.

The results show a slight increase in the case of the denatured alcohol, but the agreement for most purposes is quite satisfactory.

TESTS ON STOCK SIRUP, USING ALCOHOLS DESCRIBED ABOVE—Ten cc. of sirup, 0.5 cc. of concentrated HCl, and 50 cc. of alcohol were used. Series 2 was run with twice the acid concentration used above. The following average results were obtained:

	Grams of Gums		
Series	Ethyl Alcohol	Denatured Alcohol	Methyl Alcohol
1	0.0304	0.0301	0.0259
2	0.0301	0.0280	0.0267

The methyl alcohol gives results that are quite low on a product like black strap. The denatured alcohol is more sensitive to change in acid concentration than either the ethyl or methyl alcohol.

THE TECHNIC OF GUM DETERMINATIONS

FILTRATION OF GUMS—All the methods found in the literature, with the exception of that recommended by Noel Deerr and by Weichmann, are foreign methods, and none of the foreign methods suggest the use of a Gooch crucible. Since the ash in the gums need not be known, only two weighings are necessary when the Gooch crucible is used. This saves two weighings over tared filters, and has the further advantages of greater accuracy and ease of manipulation.

Asbestos mat Gooch crucibles are to be preferred to alundum crucibles chiefly because of the better filtration obtained with the former. Alundum crucibles are also rather difficult to wash properly. Since there is no filtration between weighings, the asbestos mat need not be washed free from fine fibers, thus making mat preparation very simple. There is a loss of only 0.0010 g. between drying and ignition, owing to asbestos and crucible losses for a mat weighing 0.20 to 0.25 g. dry. The corresponding loss for an alundum crucible is at least 0.0020 g.

EFFECT OF TIME OF STANDING AFTER PRECIPITATION ON RATE OF FILTRATION AND WEIGHT OF GUMS OBTAINED—These results were obtained from 10 cc. of stock sirup, 0.5 cc. of concentrated HCl, and 50 cc. of 94 per cent alcohol.

Expt. No.	Time of Standing before Filtration	Time for Filtering and Washing	Gums Obtained Grams
1	0 min.	4 hr.	0.0282
2	15 min.	8 min.	0.0281
3	30 min.	15 min.	0.0279
4	1 hr.	14 min.	0.0283
5	2.5 hrs.	14 min.	0.0284
6	16 hrs.	15 min.	0.0288

For filtering through asbestos mat crucibles, 15 min. standing is all that is necessary. No serious error is introduced by different times of standing.

TEMPERATURE OF DRYING AND TIME REQUIRED TO REACH CONSTANT WEIGHT—Drying at 90° C. in 30-min. periods comes to constant weight in 90 min. The precipitate goes from 0.0290 to 0.0280 g. from first to last period.

Drying at 100° C.; constant weight in 60 min.; 0.0282 to 0.0280 g.
Drying at 105° C.; constant weight in 30 min.
Drying at 110° C.; constant weight in 30 min.

Using the same gum precipitate, the drying was carried constant at 90° C., then constant at 95° C., etc., with the following results:

90° C. constant at 0.0282 g.; 90 min. required
95° C. constant at 0.0281 g.; 90 min. required
100° C. constant at 0.0277 g.; 60 min. required
105° C. constant at 0.0271 g.; 30 min. required
110° C. constant at 0.0269 g.; 30 min. required

These results show that even a 5° change in drying temperature will cause but little error. The time required to reach constant weight will also vary somewhat with the weight of the precipitate. For this reason it is desirable to dry at least 1 hr. at a temperature of 100° to 105° C.

RECOMMENDED METHOD FOR GUM DETERMINATION

SAMPLE—If the sample is a sirup or juice, dilute to or concentrate to about 50 per cent solids. For work in which only comparative results are desired on products of nearly the same density, this is not necessary but it is desirable. The sample should be free from suspended matter. We find filtering through asbestos or centrifuging fairly satisfactory. Care must be taken that no clarification that has a tendency to remove gums is used. If the gum content is low, use a 20-cc. sample; if high, use a 10-cc. sample. If the density of the sample is not accurately known, it should be weighed to the nearest 0.1 g.

A sugar can be dissolved in an equal weight of water and should usually be filtered. Sodium benzoate satisfactorily keeps sirups for gum analysis.

ACIDITY—Use 0.5 cc. of concentrated HCl for the 10-cc. sample and 1.0 cc. for the 20-cc. sample. Add the acid to the sirup; otherwise, in the case of very low-grade products an unfilterable precipitate may be obtained.

ALCOHOL—Use alcohol at about 93 to 96 per cent by volume. In case methyl or denatured alcohol is used, a large supply should be kept so that the results will be comparable. This old supply should not be entirely used before checking against the new supply on the products usually analyzed. With ethyl alcohol it is only necessary to see that the density is the same. For some products methyl or denatured alcohol will give results nearly the same as the ethyl alcohol, but on other products the results may be lower. Denatured alcohol especially should be watched, as the nature of the substance used for denaturing may be a factor in its behavior as a gum precipitant. Alcohol denatured with methyl alcohol alone is preferable for gum precipitation. All alcohol should be filtered before use.

PRECIPITATION—The precipitation is preferably conducted in 120-cc. Erlenmeyer flasks or in beakers. The alcohol should be added from a rather slow delivery pipet, and the mixture should be well agitated during the precipitation. Use 50 cc. of alcohol for the 10-cc. sample and 100 cc. for the 20-cc. sample. To avoid slow filtration allow the precipitate to stand 15 min. before filtering.

Filtration—Use an asbestos mat Gooch crucible. The mat should contain at least 0.20 g. of dry asbestos for a precipitate weighing from 0.2 to 0.5 g. It is unnecessary to wash the mat free from fine fibers or to weigh the crucible before filtering the gums. The flask containing the precipitate should be drained before rinsing, and the rinsings of wash alcohol should not be added until the last drop of the original liquor has passed through the mat. The filtration and washing of precipitates weighing about 0.01 g. ordinarily need not require more than 5 min., and precipitates of about 0.05 g. can be handled in 15 min. Alundum crucibles if used need not be weighed before filtration of the gums.

Wash Alcohol—The requirement for the wash alcohol is that it shall be of higher alcohol concentration and of less acidity than the alcohol in the mixture of sirup, alcohol, and acid. This avoids any solvent effect on the precipitate. It is advisable to use the same strength alcohol for washing as was used in precipitating the gums. Occasionally a little acid in the wash alcohol will speed up the filtration.

Drying—Dry at 100° to 105° C. for 1 hr. For very large precipitates it is well to see whether this is sufficient to give constant weight.

Weighing—After drying and ignition the crucible should be cooled in a desiccator and weighed. These weighings should be on a balance accurate to 0.0001 g.

Ignition—The ignition of the organic matter may be accomplished in a muffle or by a Bunsen flame, and must be continued until all the carbon is consumed. This usually requires 10 to 15 min. The difference between the weight after drying and after ignition represents the dried gums. For very accurate work or where the precipitate weighed is very small, a correction must be applied for the loss in weight of the dried crucible and mat during ignition. For a 14- to 18-g. Gooch crucible with a 0.20 to 0.25 g. asbestos mat, this correction amounts to 0.0010 g. This correction may be determined once for all for any crucible and mat. The mats nearly constant in weight are prepared by using the same volume of a thoroughly shaken stock suspension of asbestos and water.

Acknowledgment

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Color and Ash Absorption by Boneblack and Decolorizing Carbons[1]

By W. D. Horne

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The wide interest in decolorizing carbons and the fact that they are frequently offered as substitutes for boneblack in certain lines of work give importance to the comparison of their relative advantages in various technical applications.

Some of the carbons produced in recent years possess a remarkable color-absorbing capacity when applied to sugar solutions, and this has in some cases proved all that was needed to make them of value in some industries, and at the same time has rather diverted attention from their frequent inability to absorb much, if any, ash, which is such an important feature in sugar refining.

Ordinary Practice

In sugar refining, from 75 to 100 lbs. of boneblack are ordinarily used for the filtration of each 100 lbs. of raw sugar. This boneblack is applied in the filtration of washed sugar and washings, and to sirups from centrifugals at various stages in the process. In this way one-third to one-half of the organic impurities may be removed and one-quarter to one-third of the ash, while about three-quarters of the total color is taken out.

On the other hand, the decolorizing carbons are used in much smaller proportion to sugar, and usually vary from 3 to 10 per cent of the weight of solids in the sugar solution. They remove commonly from about two-thirds to nearly all of the color present without absorbing any notable amount of ash.

For example, in a comparative study of four commercial decolorizing carbons, 250 cc. of bag-filtered, washed sugar solution at 80° C. were added in each case to 25 cc. of the carbon, and the whole kept at 80° on the water bath, with frequent stirring, for 40 min., and then filtered. The original liquor had a color of 8, according to an arbitrary scale in which water reads 0 and a rich brown caramel solution reads 100. The four filtrates *a*, *b*, *c*, and *d* read, respectively, 1.5, 0, 3, and 1, showing removal of 81.75, 100, 62.5, and 87.5 per cent. The carbons were then washed and boiled with 10 cc. saturated solution of caustic soda diluted to 75 cc., filtered, and washed free from alkali. Then 80.5 per cent of the original weight of each of these carbons was taken, and to this were added 250 cc. of this liquor darkened with raw sugar washings, the whole heated at 80° C. on the water bath, with frequent stirring, for 40 min., and filtered. The color of this composite liquor was 55, and the filtrates were 10, 8, 32, and 14, respectively. The percentages of color removed were 81.81, 85.50, 41.81, and 74.54. The ash removal was not determined for the first filtration, but by the second filtration practically no ash was absorbed, for, while the original solution contained 0.35 per cent of ash on a dry basis, the amounts found in the filtrates, respectively, were 0.36, 0.37, 0.34, and 0.39 per cent.

Experiments to Determine Seat of Ash-Absorbing Power

A set of filtrations was conducted, using the main constituents of boneblack separately, and, for comparison, some of the original material at the same time. The original boneblack contained 8.26 per cent carbon, 0.50 per cent insoluble ash, 1.64 per cent calcium sulfate, 0.09 per cent calcium sulfide, 0.17 per cent iron, and 3.89 per cent calcium carbonate. The rest was mainly calcium phosphate. To prepare the samples, 250 g. of high-grade boneblack were digested, heated with about 2 liters of 25 per cent commercial hydrochloric acid, and the residue washed until it was neutral to litmus paper. The wet carbon and undissolved mineral matter weighed 167 g., and contained 87.95 per cent water, and 12.05 per cent carbon and mineral matter. Another weight of 250 g. of the same boneblack was carefully and thoroughly burned off in the muffle furnace, at a low reddish heat, until all combustible matter was removed. This left 227 g., or 90.80 per cent of the original weight of the char.

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[1] Presented before the Division of Sugar Chemistry at the 63rd Meeting of the American Chemical Society, Birmingham, Ala., April 3 to 7, 1922.

For the filtration test, three burets were placed in a double-walled glass box heated by an electric lamp, and 25 g. of the boneblack, for a standard of comparison, were placed in one of the burets above a cotton plug. In the second buret was put burned char weighing 22.9 g., calculated to represent the same original amount of boneblack as in the first buret. For the third tube were set aside 18.1 g. of the wet carbonaceous residue, calculated to contain as much carbon and insoluble ash as 25 g. of the original boneblack. A raw sugar solution at 40° Brix was prepared, and clarified by defecation with infusorial earth and filtering over paper. The original and the burned boneblack were covered with this liquor and allowed to stand 1 hr. at about 75° C., after which the liquor was allowed to percolate slowly through at the rate of 25 cc. per hr. As the wet carbon would have diluted the filtrate unevenly, it was mixed with 100 cc. of the sugar solution and heated near the boiling point for about 10 min., to obtain an even distribution of the 15.9 cc. of contained water with the 100 cc. of liquor. This mixture was poured into the third buret tube, and after standing an hour was drawn off in the same manner as the others. The readings were corrected for the dilution. By this procedure the following results were obtained:

		WHOLE BONE-BLACK		BURNED BONE-BLACK		CARBON[1] FROM BONEBLACK	
	ORIGINAL SOLUTION	1st 25 Cc.	2nd 25 Cc.	1st 25 Cc.	2nd 25 Cc.	1st 25 Cc.	2nd 25 Cc.
Color	103	4	20	27	60	8	16[1]
Color absorbed, per cent	...	96.10	80.58	73.80	41.78	92.30	84.50
Ash (on dry substance) per cent	2.914	1.535	2.133	2.235	2.378	2.678	...
Ash absorbed, per cent	...	47.32	26.80	23.30	18.39	8.10	...

[1] Color of liquor supernatant to the carbon. It would no longer percolate through.

Here we see that while the color removal is more vigorous by the carbon than it is by the mineral framework of the boneblack, the burned boneblack far more strikingly absorbs the ash constituents of the sugar solution. This is so very evident that we cannot wonder at the relatively insignificant ash removal by carbons.

The assumption, on the other hand, that the mineral portion exercises the predominating influence in ash absorption, is borne out by the behavior of an artificial boneblack formed by the fixation of carbon on a more or less porous earthy substratum.

ARTIFICIAL CHAR VS. BONEBLACK

In a filtration test arranged much as was the one just described, the artificial char was compared with high-grade boneblack, with the following results:

		BONEBLACK		SUBSTITUTE	
	ORIGINAL LIQUOR	1st 30 Cc.	2nd 30 Cc.	1st 30 Cc.	2nd 30 Cc.
Color	100	2	6	10	24
Color absorbed, per cent	..	98	94	90	76
Ash (on dry substance), per cent	2.81	1.84	..	2.12	.
Ash absorbed, per cent	..	34.52	..	24.60	..

If this hint is followed, we may eventually expect to be able to develop a decolorizing carbonaceous compound, which will not only take up color, but will also absorb ash. When viewed from the financial standpoint of the refiner, this is an important matter. To demonstrate the point more specifically, reference is made to a certain carbon, prepared from a by-product in manufacture, having good *color*-absorbing power, but which had no *ash*-absorbing power.

When 4 g. of this carbon were treated 7 times successively with 100 cc. of washed sugar solution without intermediate washing or revivifying, it was found to be 12 times as effective in color removal as the same weight of boneblack, the boneblack being used but once. The boneblack must be washed and revivified by heat after each use.

A refinery working 225 days a year can count on its boneblack wearing out in about 3 years. As the boneblack makes the cycle of its operations about once in 3 days, in the first year the full char will be used 75 times, in the second year two-thirds of the char will be used 75 times, in the third year one-third of the char will be used 75 times—making 150 times in all, calculated for the full char.

If boneblack can be used 150 times, it will be necessary to use this carbon through 12.5 cycles of 7 mixings with liquor in each cycle to get the same decolorizing effect. As the vegetable carbons are rather soft, they have been found to wear down under the attrition of use, and, as the grains grow smaller, gradually to choke the cloths of the filter press. It seems a fair assumption, from experience in this field, that 18 cycles of this kind would nearly exhaust the utility of most vegetable carbons. In other words, by the time this carbon has done 150 per cent as much decolorizing as an equal weight of boneblack can do in its whole life, the carbon will have been exhausted.

COMPARATIVE COSTS

On a color basis alone, then, it appears that such a carbon must not cost more than 150 per cent as much as char does per pound. The cost of boneblack can be taken at about 5 cents a pound net, as an allowance can be made for old boneblack sold on its phosphoric oxide content. This carbon, then, should not cost over 7.5 cents per lb., on a color absorption basis.

With regard to ash absorption, however, the average raw sugar contains about 0.6 per cent ash, of which the boneblack treatment removes from 0.2 to 0.3 per cent. The carbon failing to do this, the above-mentioned 0.2 per cent of ash holds back about 5 times its weight of sugar from crystallizing, or 1.0 per cent on the weight of raw sugar melted. The 0.4 per cent of ash left after char filtration is ordinarily accompanied by the production of about 4.5 per cent of final molasses. If none of the ash is removed, we might expect to have half again as much molasses; but the carbon removes organic impurities which also have a melassagenic influence, and so it is probably more nearly correct to assume that there will be about one-quarter more molasses with carbon than with boneblack.

Thus, 100 lbs. of raw sugar treated with 80 lbs. of boneblack should produce 93 lbs. of refined sugar at 5.1 cents per lb., or \$4.743, and 4.5 lbs. of molasses at 1 cent, or \$4.788 altogether. The same amount of raw sugar refined with carbon would give about 92 lbs. of sugar (\$4.692) and 5.625 lbs. of molasses at 0.8 cent per lb. (cheaper because of its higher ash content), worth 4.5 cents or \$4.737 altogether, which is 5.1 cents less than when boneblack is used. The cost of the 80 lbs. of char needed for handling 100 lbs. of raw sugar at 5 cents net is \$4.00, and if this can be used in all 150 times, the cost for a single use will be 2.66 cents. Since the boneblack thus effects a saving, compared with carbon, in refining, of nearly twice as much as the boneblack costs, it is evident that such a carbon cannot compete with it at any price.

To offset this, in erecting a plant to use carbon instead of boneblack, there would be a saving in overhead expenses, and, as revivifying processes develop, it may prove cheaper in revivification than char because of the smaller weight handled, thus diminishing operating expenses also.

The great result to achieve is the production of an ash-absorbing carbon, and from all present indications it will consist of a porous mineral foundation overlaid with a highly activated carbon, and such a material will have a great advantage if it can be handled in filter presses as the existing carbons are handled.

The Determination of Aluminium as Phosphate[1,2]

By G. E. F. Lundell and H. B. Knowles

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Determinations of aluminium as phosphate are generally in error. Acceptable determinations are possible when only a few milligrams of aluminium are involved, and high values are the rule when more than 1 to 5 mg. of aluminium are precipitated by ordinary procedures. Immoderate washing of the precipitate or the use of a weak acid wash leads to low values, as does also precipitation with only a moderate excess of the precipitant, or precipitation in alkaline solution. Under these conditions iron behaves like aluminium, while titanium invariably yields low values.

Many methods of analysis call for the determination of aluminium by precipitation, and weighing as phosphate, either alone or together with iron and titanium. The calculation of aluminium is ordinarily made on the basis of the composition $AlPO_4$, with corrections, when necessary, for iron and titanium as separately determined and calculated on the basis of the normal phosphates $FePO_4$ and $Ti_3(PO_4)_4$. Most procedures call for precipitation in acid solution, although a few specify an alkaline one; the array of wash solutions is equally broad; hot water, hot or cold ammonium nitrate, and hot dilute acetic acid are all mentioned. In most cases the methods are given with no statement as to their accuracy; in a few instances the methods are rated as of the highest accuracy; while in three researches, at least, attention has been called to the limitations of the phosphate method. One[3] states that when aluminium is boiled for 40 min. with an excess of sodium phosphate in acetic acid solution, the phosphate which is obtained approximates the formula $7Al_2O_3.6P_2O_5$ more nearly than $Al_2O_3.P_2O_5$. Another[4] claims that the phosphate precipitated by boiling a like solution for 5 min. contains P_2O_5 in excess of that called for by the formula $Al_2O_3.P_2O_5$. The third[5] points out the difficulty in properly washing the precipitate.

In view of the foregoing facts, it is considered desirable to present the following data which embody tests carried out at this Bureau in order to determine the suitability of the method for work in hand, and which demonstrate that, while the method is quite satisfactory where only small amounts (1 to 5 mg.) of aluminium are involved, it is far from reliable where larger amounts of aluminium are in question, or when iron or titanium or both are also present and precipitated as phosphates.

EXPERIMENTAL

The results of the investigation can best be summarized as in Tables I, II, and III. The aluminium, titanium, and iron solutions were all standardized by proceeding as in the method of W. Blum,[6] with correction for silica in all cases. The phosphate solutions used for precipitation were standardized gravimetrically as magnesium pyrophosphate. All precipitates were carefully ignited and finally heated to constant weight at approximately 1000° C. In many cases macerated paper was used in an attempt to facilitate the filtering and washing of the precipitate and to obtain a finer grained ignited residue and greater ease in expelling any volatile matter.

In Table I an aluminium chloride solution was used in Expts. 1 to 8 and 15 to 22, and an aluminium nitrate solution in Expts. 9 to 14. The precipitant in Expts. 1 to 8 was sodium ammonium hydrogen phosphate, in Expts. 14, disodium hydrogen phosphate, and in the others, diammonium hydrogen phosphate. Precipitation was in acetic acid solution, except in Expt. 10 where the solution was made just alkaline to methyl orange with ammonia, and in Expt. 11 where an excess of 5 cc. of ammonium hydroxide (sp. gr. 0.90) per 100 cc. was used.

The data of Table I show that all the methods proposed for the determination of aluminium as phosphate are subject to error; those are of the least concern where only small amounts (1 to 5 mg.) are involved. Low values are the rule: (1) when less than five times the theoretical requirement of the precipitant is used; (2) when the precipitation is performed in alkaline solution; (3) when the precipitate is washed immoderately with hot or cold water or ammonium nitrate solution; or (4) when dilute acetic acid is used as a washing medium. High values are invariably obtained with moderate amounts of aluminium when over five times the theoretical requirement of precipitant is employed in acetic acid solution. This holds true regardless of whether the precipitate is washed moderately (with 300 cc. of solution) or until it is free from chlorides with hot water or hot or cold ammonium nitrate solution, or of what ignition temperatures are employed.

There seems to be little hope that a normal phosphate can be obtained by any method. The formula $3Al_2O_3$.-

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[1] Received May 22, 1922.

[2] Published by permission of the Director of the Bureau of Standards.

[3] T. M. Drown and Alex. G. McKenna, *Chem. News*, **64** (1891), 194.

[4] In the "Report of the Committee on Research and Analytical Methods —Phosphate Rock," THIS JOURNAL, **3** (1911), 787, the conclusions are given: "In order that the ignited phosphates may contain enough phosphoric acid to form the normal phosphate, it is absolutely necessary that the second precipitation, either in the acetate, Glaser, or thiosulfate method, be made in the presence of an excess of phosphoric acid." "It is impossible to exactly wash out the excess of phosphoric acid, leaving only the normal iron and aluminium phosphates." "It is possible, though hardly practicable, to remove by ignition all excess of phosphoric acid from a precipitate of aluminium phosphate without reducing the normal aluminium phosphate." "It is difficult, and the results are very uncertain at best, to remove the excess of phosphoric acid from a precipitate of iron phosphate without reducing, or, rather, driving off some of the phosphoric acid from the compound." "It is the opinion that any of the methods based on ignition of the phosphate is subject to the above-mentioned errors and uncertainties." These qualifications are not embodied, however, in the final committee report, THIS JOURNAL, 7 (1915), [illegible].

[5] J. M. Camp, *Iron Age*, **66** (1900), 17, says: "One disadvantage of the phosphate method is that there is no end-point to the washing of the precipitate, it being slightly soluble in the wash water."

[6] *J. Am. Chem. Soc.*, **38** (1916), 1282.

TABLE I—DETERMINATION OF ALUMINIUM AS PHOSPHATE

Expt. No.	P_2O_5 Added Theory Al_2O_3 P_2O_5	Amount of Washing Medium[1]	Al_2O_3 Taken G.	Al_2O_3 Found Calcd. on Basis of $AlPO_4$ G.[1]	Error G.	Error Per cent	Method
1	1	500 cc. hot H_2O	0.0861	0.0770[1]	−0.0091	−10.6	[illegible] mans Green & Company
2	1	500 cc. cold 2 per cent NH_4NO_3	0.0861	0.0776[1]	−0.0085	−9.9	
3	3	500 cc. hot H_2O	0.0861	0.0846	−0.0015	−1.7	
4	3	500 cc. cold 2 per cent NH_4NO_3	0.0861	0.0851	−0.0010	−1.2	
5	5	500 cc. hot H_2O	0.0861	0.0874	+0.0013	+1.5	
6	5	500 cc. cold 2 per cent NH_4NO_3	0.0861	0.0867	+0.0006	+0.6	
7	10	500 cc. hot H_2O	0.0861	0.0890	+0.0029	+3.4	
8	10	500 cc. cold 2 per cent NH_4NO_3	0.0861	0.0907	+0.0046	+5.3	
9	10	300 cc. hot 2 per cent Acetic	0.0485	0.0425[1]	−0.0060	−12.4	[illegible]
10	10	300 cc. hot H_2O	0.0485	0.0454[1]	−0.0031	−6.4	[illegible]
11	10	300 cc. hot H_2O	0.0485	0.0367[1]	−0.0118	[illegible]	Slightly more alkaline than the above
12	1	300 cc. hot 5 per cent NH_4NO_3	0.0485	0.0446	−0.0039	−8.0	Expt. 12 illustrates the effect of in- [illegible]
13	5	300 cc. hot 5 per cent NH_4NO_3	0.0485	0.0516	+0.0031	+6.4	[illegible] 7 (1915), 446. Scott "Standard Methods of Chemical Analyses," D. Van Nostrand Company, 2nd ed., p. 320
14	20	300 cc. hot 5 per cent NH_4NO_3	0.0485	0.0523	+0.0038	+7.8	
15	10	500 cc. hot 5 per cent NH_4NO_3	0.0471	0.0482	+0.0011	+2.3	
16	10	1000 cc. hot 5 per cent NH_4NO_3	0.0471	0.0459	−0.0012	−2.6	
17	10	2000 cc. hot 5 per cent NH_4NO_3	0.0471	0.0445[2]	−0.0026	−5.5	The washings in Expt. 17 contained only traces of Al_2O_3 while those of Expt. 18 contained less than 1 mg. of Al_2O_3
18	10	2000 cc. hot H_2O	0.0471	0.0394[2]	−0.0077	−16.4	
19	10	175 cc. hot 5 per cent NH_4NO_3	0.0019	0.0019	±0.0000	0	As in previous method, only precipitates were washed until entirely free from chlorides
20	10	175 cc. hot 5 per cent NH_4NO_3	0.0094	0.0096	+0.0002	+2.1	
21	10	550 cc. hot 5 per cent NH_4NO_3	0.0943	0.0964	+0.0021	+2.2	
22	10	600 cc. hot 5 per cent NH_4NO_3	0.1886	0.1930	+0.0044	+2.3	

[1] Considerable aluminium in filtrate.

[2] The weighed residue obtained in Expt. 17 gave when analyzed 45.33 per cent Al_2O_3 and 53.88 per cent P_2O_5, while that obtained in Expt. 18 gave 50.16 per cent Al_2O_3 and 48.58 per cent P_2O_5, as against the theoretical values of 41.79 per cent Al_2O_3 and 58.21 per cent P_2O_5 for $AlPO_4$. These values, in conjunction with the negligible alumina recoveries from the washings, illustrate the progressive hydrolysis of the precipitate and the washing out of phosphoric acid.

$4P_2O_5.18H_2O$ represents very closely the composition of aluminium phosphate precipitates, obtained by the use of an excess of phosphate in either acetic acid or ammoniacal solution, with preliminary drying with blotting paper, final drying in the air, and correction for all impurities. Washing this compound progressively removes phosphorus, with little, if any, aluminium, even after the "$AlPO_4$" stage has been reached.

Expts. 19 to 22 show that desirable modifications of the official method[7] consist in precipitating in the presence of macerated paper, and final washing of the phosphate until it is free from chlorides.

TABLE II—BEHAVIOR OF IRON IN THE OFFICIAL METHOD

(Determinations made with a solution of ferric sulfate as in the official method,[7] except as to varying the amount of diammonium hydrogen phosphate precipitant as noted in Column 1)

Expt. No.	P_2O_5 Added Theory Al_2O_3:P_2O_5	Fe_2O_3 Taken G.	Fe_2O_3 Found Calc. on Basis of $FePO_4$ G.	Error Fe_2O_3 G.	Error Fe_2O_3 Per cent
1	1	0.0530	0.0503	−0.0027	−5.1
2	1	0.0533	0.0503	−0.0030	−5.6
3	5	0.0582	0.0607	+0.0025	+4.3
4	5	0.0505	0.0519	+0.0014	+2.8
5	20	0.0537	0.0565	+0.0028	+5.2
6	20	0.0564	0.0594	+0.0030	+5.3

The data show that iron behaves like aluminium, and that it will increase the errors in any aluminium determinations where both are precipitated and aluminium then obtained by difference after a separate determination of the iron and deduction as calculated $FePO_4$. For example, in such a procedure a rock containing 10 per cent of Fe_2O_3 and no aluminium would appear to have somewhere in the neighborhood of 0.20 per cent of Al_2O_3 on the basis of Expts. 5 and 6. In the official method, a known amount of iron is added to the solution of the material and a like amount carried through as a *blank*, which is afterward subtracted together with the theoretical $FePO_4$ equivalent of the iron in the material as separately determined. As the actual blank is quite small, a more satisfactory procedure would lie in computing the $FePO_4$ equivalent of the iron in the material on the basis of the actual performance of the known amount of iron in the blank.

TABLE III—BEHAVIOR OF TITANIUM BY THE OFFICIAL METHOD

(Determinations made by precipitating an acetic acid solution of titanic sulfate as in the official method[7] except as to varying the amount of diammonium hydrogen phosphate precipitant, as noted in Column 1)

P_2O_5 Added Theory Al_2O_3 P_2O_5	TiO_2 Taken G.	TiO_2 Found Calc on Basis of $Ti_3(PO_4)_4$ G.	Error TiO_2 G.	Error TiO_2 Per cent
1	0.0528	0.0424	−0.0104	−19.7
1	0.0528	0.0422	−0.0106	−20.1
5	0.0528	0.0456	−0.0072	−13.6
5	0.0528	0.0455	−0.0073	−13.8
20	0.0528	0.0485	−0.0043	−8.1
20	0.0528	0.0473	−0.0055	−10.4

The data here show that titanium consistently yields low values in the phosphate method, and that when aluminium is obtained by difference after a separate determination of titanium and deduction as calculated $Ti_3(PO_4)_4$, small amounts of titanium will offset the normally high values obtained for aluminium, as in Tables I and II, while large amounts of titanium will cause low values. Where titanium is present and ignored, as is usually the case, it will of course add to the high value obtained for aluminium.

The data presented in Tables I, II, and III demonstrate that values for aluminium which are obtained by such methods as that of Peters, and the one recommended by the Fertilizer Division of the AMERICAN CHEMICAL SOCIETY will normally be high in case more than a few milligrams of aluminium are involved; that the values will be higher still when iron is also involved, as in the latter method; and that the values will be lowered by titanium (provided it is considered) in proportion to the amount present.

The degree of Bachelor in Colour Chemistry has been created at the Manchester College of Technology, Manchester, England. Dr. F. M. Rowe, editor of the *Colour Index* now being issued by the Society of Dyers and Colourists, who is in charge of this work, states that students are being encouraged to carry out some of their experiments in a miniature plant, because although the dyestuffs industry is now staffed to capacity with the large numbers who entered it during the war, new research workers will be needed as dye making develops in Great Britain.

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[7] Recommended by the Fertilizer Division of the American Chemical Society, THIS JOURNAL, 7 (1915), 446. See Table I, Expts. 13 and 14 of this article.

Alumina as an Absorbent for Water in Organic Combustions[1]

By H. L. Fisher, H. L. Faust and G. H. Walden

Columbia University, New York, N. Y.

In this paper the preparation of alumina is described with special reference to its use in the absorption train for organic combustions, its advantages over other absorption agents pointed out, and the results of several analyses given.

In 1912, Johnson[2] published a note on "Alumina as a Drying Agent," in which he showed that alumina, prepared by heating aluminium hydroxide in a tube at a "low temperature," was as efficient as phosphorus pentoxide for drying purposes. At that time one of us was working on some problems in connection with organic combustions. Since aluminium does not form a stable carbonate, aluminium oxide and hydroxide ought not to absorb carbon dioxide, and therefore the supposition was made that it should be an excellent substitute for anhydrous calcium chloride in the absorption train for organic combustions. Our work, which was begun in 1916, has proved that this supposition is correct. In the meantime, two other articles have appeared dealing with the efficiency of alumina[3] in ordinary work as compared with calcium chloride and other drying agents.[4] After the major portion of our work was finished, it was found that alumina had also been used by Wesson[5] in the absorption train for combustions, but only to take up the moisture given off from the moist soda lime used for absorbing the carbon dioxide in determining the carbon in the nitrosite of rubber. The hydrogen in this case was not wanted and was not determined, concentrated sulfuric acid being used simply to remove the water formed in the combustion.

Preparation of the Alumina

From Aluminium Hydroxide—Ten grams of pure aluminium hydroxide were shaken up with 2 g. of purified and ignited asbestos. The asbestos was added to give greater porosity. The mixture was heated in a 7.5 cm. quartz dish over a nonluminous flame 5 cm. high, for 1.5 hrs. During the first half-hour the material lost 3.101 g., the second, 0.068 g., and the third, 0.014 g. On standing over night in a desiccator containing concentrated sulfuric acid, it gained 0.018 g. This mixture gave excellent results.

The aluminium hydroxide must be free from alkali. When mixed with neutral water it should give only the faintest color with phenolphthalein.[6] The mixture can be used over again simply by heating it once more under the same conditions. It cannot, however, be reheated very often since the asbestos soon crumbles to a powder.

From Hydrated Aluminium Chloride—The alumina as made by the method just outlined tends to pack readily, and then it sometimes requires 3 to 4 hrs. for the complete passage of the carbon dioxide through it. On this account pumice was used in place of the asbestos and the alumina itself prepared in a different way, as follows: 50 g. of hydrated aluminium chloride ($AlCl_3.6H_2O$) were dissolved in 100 cc. of warm water in a 11.5-cm. quartz dish and 50 cc. (about 24 g.) of 12-mesh pumice stirred in. It has to be well stirred with a stout glass rod, especially after most of the water has disappeared, since the mixture foams a good deal and tends to form a cake. The particles of pumice should be kept separated as much as possible. The heating and stirring were continued until there was no danger of later fusion of the hydrated salt and agglomeration of the small lumps of impregnated pumice. This material was then transferred to a 7.5-cm. quartz dish and heated in an electric muffle furnace to 700° to 750° C. until no more hydrogen chloride was given off. A higher temperature should not be used since alumina when prepared at higher temperatures no longer absorbs water.[7] The time of heating can be shortened to 30 to 45 min. if a stream of air is blown or drawn through the heating chamber to remove the gaseous products. At the end of the heating the dish was allowed to cool in a desiccator that had no drying agent in it. If the heating is too long or too high the alumina will no longer cling to the pumice, but will drop off as a fine powder. It will do this to some extent under any conditions.

Alumina as a Drying Agent

According to Johnson[2] the alumina is an excellent drying agent up to the time that it has absorbed about 18 per cent of its weight of water at the ordinary temperature. Fifty grams of hydrated aluminium chloride theoretically yield about 10.7 g. of aluminium oxide, and this amount ought to absorb about 1.92 g. of water under ideal conditions. If we consider the average organic substance as containing about 5 per cent of hydrogen, then a 0.2 g. sample will yield approximately 0.09 g. of water, and on this basis the aluminium oxide theoretically ought to suffice for 21 combustions. In practice we have not used the mixture for more than 4 to 5 combustions.

Since alumina is as efficient a drying agent as phosphorus pentoxide, it must be handled accordingly, even though it gives no outward change in appearance when absorbing moisture.

The material was tested out in a practical way for absorbing the water formed in the combustion of several organic substances. The oxygen for the combustions was purified by passing it through a preheater followed by soda lime and alumina. Blank determinations were run in each case and excellent checks obtained before the substance itself was burned. The carbon dioxide was absorbed by soda lime and this was followed by a second lot of the alumina in order to insure the complete absorption of the moisture from the soda lime. Anthracene was chosen for the first trials on account of its high carbon content. The theoretical percentage of hydrogen in anthracene is 5.66, and the first three results were 5.55, 5.61, and 5.49 per cent. Further results on this and other substances are given below:

SUBSTANCE	Formula		Hydrogen Per cent	Carbon Per cent	REMARKS
Anthracene	$C_{14}H_{10}$	Calcd.	5.66	94.34	
		Found	5.71	94.17	Alumina - asbestos used
			5.57	94.36	Alumina - pumice used
			5.53	94.12	
Salicylic acid	$C_7H_6O_3$	Calcd.	4.38	60.84	
		Found	4.47	60.77	Alumina - pumice used
			4.38	60.82	
Cane sugar	$C_{12}H_{22}O_{11}$	Calcd.	6.46	42.09	
		Found	6.48	42.05	Alumina - asbestos used
			6.46	42.14	

The advantages of alumina over other absorption agents in organic combustions are as follows:

Concentrated Sulfuric Acid—The alumina is a solid and therefore it is easier to handle, and it offers much less resistance to the passage of the gases. Furthermore, less weight can be used.

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[1] Received July 31, 1922.

[2] *J. Am. Chem. Soc.*, **34** (1912), 911.

[3] Marden and Elliott, This Journal, **7** (1915), 320; Dover and Marden, *J. Am. Chem. Soc.*, **39** (1917), 1609.

[4] Baxter and Warren, *J. Am. Chem. Soc.*, **33** (1911), 340; Baxter and Starkweather, *Ibid.*, **38** (1916), 2038; A. T. McPherson, *Ibid.*, **39** (1917), 1317.

[5] This Journal, **6** (1914), 461; **9** (1917), 59.

[6] Compare the curve in article by Blum, *J. Am. Chem. Soc.*, **35** (1913), 1499.

[7] Dammer, "Handbuch der anorganischen Chemie," **3** (1893), 89.

CALCIUM CHLORIDE—(1) The alumina mixed with the abestos or the pumice exposes a greater surface. (2) The same bulk weighs less. (3) When it has absorbed water it does not form crystalline hydrates which "freeze" to the walls of the absorption bottle. (4) It contains no basic substances which introduce an inconstant error, and therefore it need not be saturated with carbon dioxide before using.

PHOSPHORUS PENTOXIDE—The alumina becomes a hydroxide of aluminium, which is a solid and therefore does not clog the apparatus as does the phosphoric acid formed from phosphorus pentoxide.

A Rapid Method of Analysis for Dolomite and Magnesian Limestone[1]

By S. D. Averitt

KENTUCKY AGRICULTURAL EXPERIMENT STATION, LEXINGTON, KY

IN THE analysis of dolomite and magnesian limestone for agricultural and commercial uses, a quick, easy, and fairly accurate method of finding the amount of calcium carbonate and magnesium carbonate present is very desirable.

In this paper is given an indirect method which meets those requirements and seems to be generally applicable to that class of stones. The functions concerned are: (1) neutralizing power of the stone as calcium carbonate, A; (2) insoluble residue and ammonium precipitate, B; (3) moisture, M. It does not involve the determination of either calcium or magnesium, and is fully as accurate and somewhat shorter than the usual differential method, which, in addition to the neutralizing power as calcium carbonate, requires the actual determination of calcium.

In the following table a summarization is given of the data obtained on 20 representative samples of magnesian limestones and dolomites:

TABLE I

	$MgCO_3$		$CaCO_3$			B + M[1]	
No.	Indirect	Differential	Indirect	Differential	A	B	M
1	35.80	35.70	48.80	48.80	91.30	15.2	0.20
2	8.99	8.85	87.68	87.82	98.35	3.26	0.07
3	31.80	31.88	63.26	63.05	101.00	4.92	0.02
4	33.76	33.64	57.28	57.30	97.35	8.84	0.12
5	38.80	38.60	49.95	50.00	96.00	11.18	0.07
6	34.50	34.50	56.40	56.30	97.40	8.94	0.11
7	40.70	40.60	56.50	56.50	104.80	2.74	0.06
8	34.80	34.80	50.10	50.04	91.40	14.9	0.20
9	42.30	42.00	54.80	55.04	105.00	2.84	0.06
10	5.08	5.04	89.60	89.60	95.60	5.28	0.07
11	35.30	35.40	62.30	62.05	104.20	2.32	0.08
12	26.50	26.40	70.05	70.06	101.50	3.40	0.05
13	33.70	33.50	59.60	59.70	99.60	6.62	0.08
14	39.05	38.90	49.85	49.90	96.20	10.90	0.20
15	35.80	36.20	54.60	54.04	97.10	9.48	0.12
16	5.10	5.04	92.05	92.10	98.10	2.80	0.05
17	41.50	41.40	55.25	55.25	104.50	3.20	0.05
18	3.20	3.20	89.50	89.50	93.30	7.22	0.08
19	11.80	11.70	79.90	80.00	93.90	8.24	0.06
20	38.00	37.80	60.50	60.55	105.60	1.46	0.04

[1] Assumed except in Nos. 2, 3, and 4.

The figures for $MgCO_3$ in the column marked "Indirect" were calculated from the equation:

$$\Big[A - \Big(100 - (B + M)\Big)\Big]\, 5.35 = MgCO_3$$

which expresses the relation of magnesium carbonate ($MgCO_3$) to the neutralizing power of the stone as calcium carbonate, the insoluble residue and ammonium precipitate, and moisture in dolomite and magnesian limestone.

The factor 5.35 is derived as follows: Taking as known quantities $a = 2.274$ and $b = 1.916$, the factors for converting CO_2 into $CaCO_3$ and $MgCO_3$, respectively, and taking as unknown quantities, X representing the percentage of total CO_2 in the sample combined as $CaCO_3$ and Y representing the percentage combined as $MgCO_3$, we may write the following equations:

$$aX + bY = 100 - (B + M) \qquad (1)$$

$$aX + aY = A \qquad (2)$$

Solving for Y and getting BY($MgCO_3$) we have

$$bY = \left[A - \left(\frac{100 - (B + M)}{a - b}\right)\right]b \qquad (3)$$

Substituting for BY, $MgCO_3$, and for $\frac{b}{a-b}$ its value 5.35, we have

$$\Big[A - \Big(100 - (B + M)\Big)\Big]5.35 = MgCO_3 \qquad (4)$$

Using Equation 4 in connection with the following equation:

$$100 \text{ Per cent} - (B + M) = \text{Per cent } CaCO_3 + \text{Per cent } MgCO_3 \quad (5)$$

which is self-evident, the percentage of calcium carbonate ($CaCO_3$) and magnesium carbonate ($MgCO_3$) in the sample can be readily calculated.

A comparison of the figures in Table I for calcium carbonate ($CaCO_3$) and magnesium carbonate ($MgCO_3$) by the indirect and the differential methods shows that they are of about equal accuracy. In connection with this statement it should be noted that the calcium carbonate in the column marked "Differential" was actually determined. The method here given has been checked against the differential method on more than 50 samples of magnesian limestone containing from 3.2 per cent to 42.8 per cent $MgCO_3$ and of varying degrees of impurity. The maximum difference was 0.5 per cent $MgCO_3$. The average was slightly more than 0.1 per cent. This shows as close agreement as could be expected and indicates a reasonably wide applicability of the method.

DETAILS OF THE EXPERIMENTAL PROCEDURE

One-half gram of finely ground stone is put into a widemouth flask of 100- to 150-cc. capacity and 25 cc. 0.5 *N* HCl added, and the sides of the flask washed down with a little water. It is then boiled gently 5 or 10 min., or until decomposition of $CaCO_3$ and $MgCO_3$ is complete. Enough hot water to maintain or slightly increase the volume is used once or twice during the boiling to wash down the sides of the flask. The solution is then cooled and the excess acid neutralized with 0.25 *N* NaOH, a small drop of methyl orange being used as the indicator, and the first change from pink to yellowish is taken as the end-point. Note exactly the volume of 0.25 *N* NaOH required to neutralize the excess acid. To the solution add 10 cc. of 10 per cent NH_4Cl solution and two drops of ammonia, heat gently until the

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[1] Received September 21, 1921. Accepted October 7, 1922. Presented before the Lexington Section of the American Chemical Society, December 15, 1920.

ammonia precipitate flocculates. Filter the precipitate and insoluble residue on a washed, dried, and weighed filter; wash thoroughly with hot water, dry at 100° to 105° C., and weigh. The difference is the weight of insoluble residue and ammonia precipitate.

To the percentage of insoluble residue and ammonia precipitate a small correction for moisture, M, must be added. This correction is from 0.02 to 0.05 per cent for pure stones, up to 0.15 per cent and even 0.20 per cent for those containing considerable amounts of insoluble residue.

A clayey insoluble residue contains more moisture than a sandy one, and its character should be noted as a guide to the worker in the assumption of moisture correction.

From the titration calculate the calcium carbonate ($CaCO_3$) equivalent of the acid neutralized by the stone, as per cent $CaCO_3$, A. The percentage of insoluble residue and ammonia precipitate, B, having been determined, and the moisture, M, assumed, we are able to use Equations 4 and 5 as stated above.

The moisture was determined on the samples in Table I subsequent to the assumptions, except in Nos. 2, 3, and 4 as noted, and in no case was the difference more than 0.03 per cent and in a large majority only 0.01 and 0.02 per cent, from which it is evident that, with due regard to the character of the insoluble residue, the moisture may be assumed without material error.

Colloiding Agents for Nitrocellulose[1,2]

By Tenney L. Davis

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Certain nonvolatile solvents for nitrocellulose, either incorporated throughout the mass of the grain or applied to the exterior as a surface coating, are used in the manufacture of colloided smokeless powder. Their value lies in the fact that they reduce the amount of volatile solvent needed in the manufacture, and that they influence the rate of burning of the finished powder and determine its attitude toward moisture. The present paper is a report of a study of the solvent action of a number of ureas, urethanes, and sebacic and phthalic esters. Results are such as to permit inferences regarding the relation between structure and solvent action.

WHEN colloided *straight nitrocellulose* powder is exposed to a moist atmosphere, it takes up moisture for two reasons, because of the hygroscopicity of the colloid itself and because of the considerable hygroscopicity of the ether-alcohol that is still retained in the material of the powder grain. Since the moisture so taken up impairs the ballistic properties of the powder, a study of the mechanism of the process by which it is absorbed and of the means by which that process may be regulated or prevented is of obvious interest.

We have shown[3] that the absorption of moisture by colloided straight nitrocellulose powder produces precipitation of the nitrocellulose and is accompanied by the production of minute cracks or pores in the surface of the grain. If the powder, after exposure to moisture, is now desiccated, the moisture held in these cracks by capillary action is driven off, the cracks give access to the residual ether-alcohol in the interior of the grain and some of this is also driven off, with the result that the desiccation of the powder actually drives off more volatile matter than the powder had taken up during its exposure to the moist atmosphere. By repeated exposure to moisture and subsequent desiccation, the powder soon reaches a condition of being *perfectly porous;* it no longer contains any ether-alcohol, and the gains and losses on successive exposures and dryings are equal. The amount of moisture which the powder now takes up is a measure of the true hygroscopicity of the ether-alcohol-free material of the powder grain, and, naturally, is considerably less than would be taken up under similar conditions by the original powder grain.

In certain coated or *progressive burning* powders, the exterior of the grain has been toughened and slowed down in its rate of burning by treatment with some colloiding agent. *Centralite*, or *sym*-dimethyl diphenylurea, has been much used for the purpose. Suitable colloiding agents are nonvolatile or high-boiling substances, they are nonhygroscopic and capable of forming with the surface of the powder grain a skin of reduced hygroscopicity which protects the ether-alcohol of the interior of the grain from taking up the moisture which it would otherwise attract.

In a study of coated powders it has seemed proper to determine the amount of the various colloiding agents necessary for the complete gelatinization of a given amount of nitrocellulose. The results are such as to permit certain generalizations concerning the relation of the structure of the organic compound to its solvent action for nitrocellulose. We find also—a fact which does not seem to have been noted heretofore—that the amount of the colloiding agent necessary for complete gelatinization is in general different when different solvents are used for applying it to the nitrocellulose.

DISCUSSION OF EXPERIMENTS

The experimental procedure was one suggested by Marius Marqueyrol,[4] Inspector General of Powders of France, who has used it, with alcohol, for studying the action of a large number of colloiding agents on the soluble and insoluble nitrocotton that are used by the French for the manufacture of smokeless powder. We have worked in general with different colloiding agents and have studied the *pyrocellulose* which is standard for United States powder—a nitrocellulose containing 12.60 per cent nitrogen and completely soluble in ether-alcohol. When we have worked with the same materials, our results have been in close agreement with those of M. Marqueyrol for soluble nitrocotton.

Half-gram samples of dry finely pulped pyrocellulose were weighed into 30-cc. beakers, and to each sample a known weight of the colloiding agent previously dissolved in an appropriate amount of solvent (15 to 30 cc.) was added.

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[1] Received June 28, 1922.

[2] This investigation was carried out in connection with a contract between the Ordnance Department and the Massachusetts Institute of Technology, and the present paper is published by permission of the Chief of Ordnance. The author was assisted in this work by Spencer W. Prentiss

[3] Army Ordnance, II, 9 July–August 1921.

[4] Recently published, Marqueyrol et Florentin, *Mémorial des Poudres*, **18** (1921), 150, 163. These investigators worked at 35° C.

The beakers were then suspended in a specially constructed water bath which was maintained at 60° C., and the solvent was evaporated off. During the evaporation each beaker was covered with a watch glass supported on pieces of bent glass rod. It was noticed that the amount of apparent gelatinization increased rapidly during the evaporation of the last portions of the solvent, and that it was increased still further by continued heating for ten minutes or so after all the solvent had disappeared. After the evaporation, the contents of the beakers were examined carefully; some were found to be gelatinized, some not. Other samples were then weighed out and evaporated, with varying amounts of the colloiding agent intermediate between the amount which just produced complete gelatinization and the amount which just failed to do so, until the amount necessary for the complete gelatinization of half a gram of pyrocellulose had been determined to the nearest tenth of a gram, and in a few cases nearer than that.

Results, as reported, for the amount of colloiding agent necessary for the complete gelatinizing of 100 parts by weight of pyrocellulose, are therefore accurate to the nearest ten parts plus or minus. It is believed that this degree of precision is sufficiently high for ordinary purposes. If greater precision is needed, the experimental procedure that we have used will undoubtedly be adequate.

The first series of experiments was carried out with the colloiding agent dissolved in alcohol. In cases where sufficient of the material was available and where the material was soluble in benzene and ligroin, experiments were also carried out with these solvents.

In the case of the liquid colloiding agents an excess of the material simply produced a softer and softer jelly. In the case of the solids definite proportions appeared to be necessary for the production of a homogeneous mass; if insufficient was taken, part of the nitrocellulose remained unaffected; if an excess was used, the excess appeared to be deposited as such, as a second phase, and did not amalgamate with the nitrocellulose colloid.

The results are tabulated below.

PARTS OF COLLOIDING AGENT NECESSARY FOR THE COMPLETE GELATINIZATION OF 100 PARTS BY WEIGHT OF PYROCELLULOSE

SUBSTANCE	IN ALCOHOL	IN BENZENE	IN LIGROIN
Methylurea	No action with 100 parts		
Ethylideneurea	No action with 100 parts		
Sym-dimethylurea	60	70	...
Sym-diethylurea	50	50	..
Unsym-diethylurea	No action with 100 parts		
Tetramethylurea	80	...	...
Benzylurea	No action with 100 parts		
Sym-diphenylurea	No action with 100 parts		
Sym-ditolyl (p,p')urea	No action with 100 parts		
Unsym-diphenylurea	No action with 100 parts		
Triphenylurea	.	35	...
α,α-Diphenyl-p-tolylurea		40	. .
Tetraphenylurea	No action with 160 parts	30	. .
Ethyltriphenylurea	80	...	...
Sym-dimethyldiphenylurea	70	26	...
Sym diethyldiphenylurea	70	30	.
Sym-dibutyldiphenylurea	60	20	...
Unsym-dimethyldiphenylurea	60	.	...
Carbamic acid ethyl ester	140	80	...
Methyl carbamic acid ethyl ester	90	60	...
Ethyl carbamic acid ethyl ester	90	60	...
Phenyl carbamic acid ethyl ester	20	90	.
Phenyl carbamic acid phenyl ester	No action with 200 parts		
Phenyl carbamic acid benzyl ester	No action with 100 parts		
Diphenyl carbamic acid phenyl ester	80	70	...
Methyl sebacate	80	70	105
Ethyl sebacate	80	50	90
Isoamyl sebacate	70	95	90
Methyl phthallate	95	70	115
Ethyl phthallate	95	50	100
Isoamyl phthallate	95	50	80
DNX oil	120	130	330

CONCLUSIONS

In general, the amount of colloiding agent necessary for the complete gelatinization of pyrocellulose is greater if the substance is applied by means of its solution in alcohol than if applied in benzene solution, and is less than if applied in ligroin solution.

Of the alkylated ureas, those in which there is only one alkyl group or in which two alkyl groups are unsymmetrically disposed appear to be without action on pyrocellulose.

Alkylated ureas in which two alkyl groups are symmetrically substituted are excellent solvents, and the property remains even if other aliphatic or aromatic groups are substituted in the molecule. The heavier the alkyl groups, the greater appears to be the gelatinizing power.

Of the aromatic substituted ureas, those in which there are less than three aromatic groups appear to be without action.

In the case of the alkyl esters of sebacic and phthalic acids, the heavier the alkyl group the better, in general, appears to be the gelatinizing action.

Alkyl esters of aliphatic and of aromatic substituted carbamic acid are excellent solvents, while the aromatic esters appear to be without action unless the total number of aromatic groups is equal to three.

Directory of Societies for Chemists

A directory of the names and addresses of the secretaries of the leading chemical societies, and other organizations bordering thereon, is given below in the hope of meeting the needs of those desiring such information:

AMERICAN CERAMIC SOCIETY: Ross C. Purdy, Ohio State University, Columbus, Ohio.

AMERICAN CHEMICAL SOCIETY: Charles L. Parsons, 1709 G St., N. W., Washington, D. C.

AMERICAN ELECTROCHEMICAL SOCIETY: Colin G. Fink, Columbia University, New York, N. Y.

AMERICAN INSTITUTE OF CHEMICAL ENGINEERS: John C. Olsen, Polytechnic Institute, Brooklyn, N. Y.

AMERICAN INSTITUTE OF FERTILIZER CHEMISTS: W. J. Gascoyne, Jr., 27 So. Gay St., Baltimore, Md.

AMERICAN LEATHER CHEMISTS ASSOCIATION: H. C. Reed, 22 East 16th St., New York, N. Y.

AMERICAN OIL CHEMISTS SOCIETY: Thomas B. Caldwell, Law & Co., Wilmington, N. C.

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Photosynthesis and the Possible Use of Solar Energy[1]

By **H. A. Spoehr**

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The purpose of the following brief outline is to show that while the photosynthetic process of the plant is at present the only means we have of utilizing solar energy, this method is so very inefficient and subject to such great uncertainties that it is exceedingly doubtful whether it can be depended upon to maintain our energy requirements. In other words, our civilization is using energy at a prodigious rate, and we would be depending upon the exceedingly inefficient and slow process of photosynthesis to supplant the supplies which have been stored for centuries and are now being depleted. Add to this, that in order to supply food for our increasing population, no encroachment on agricultural industry would be permissible. Theoretical speculations of the nature of what might be accomplished if, for instance, all the arable land were cultivated, are of no consequence to the problem. Conditions, economic and social, must be faced as they exist. The inertia of our civilization is such that great changes are induced only by the labored movements of evolution or by catastrophe. What part, then, can science and engineering play in the solution of this problem?

First of all, it is the function of scientists to exercise foresight in matters regarding the material welfare of humanity. The experiences of the various scientific bodies called together to cope with the many problems incident to the war, concur in the conclusion that very rarely is necessity the parent of invention where difficult and highly complex problems are concerned. So for this work there will be required an enormous amount of patient labor, which naturally should be begun long before the situation becomes acute.

IT HAS frequently been said of our earth that there are no exports and no imports aside from occasional meteorites. This is true as far as matter is concerned, but it is not true when energy is considered. Matter and energy are the two fundamental entities in our conceptions of all physical phenomena. As scientific thought progresses, ever-increasing attention is being given to the paramount importance of energy relations in the interpretation of natural phenomena. Matter is of interest to us largely in so far as it exhibits certain properties and undergoes definite changes. In viewing the common materials upon which we depend for the maintenance and propagation of life, it is evident that we are less interested in the matter as such than its ability to undergo certain changes which contribute in one way or another to our life activities. From this practical viewpoint, knowledge of the composition of coal, iron ore, sugar, etc., has its ultimate interest in guiding us in the application of such materials to the manifold needs of our complicated physical and physiological economy.

The eminent physicist Boltzmann pointed out in his classical exposition of the second law of thermodynamics that the struggle for existence is essentially not a fight for the raw materials that are abundant in earth, sky and sea, nor for the energies as such, but for the potential energies as in coal, sugar, and meat. Thus energetics commands the center of attention in the consideration of the chemical phenomena exhibited by the various forms of matter, and matter is but a medium for the manifestation of energy.

If our earth were an isolated system in which there were no imports and no exports, our state of affairs would be very different from that which now presents itself to us. According to our experience, formulated in the laws of thermodynamics, in all naturally occurring transformations there is a tendency to arrive at a condition of stable equilibrium. Thus, the substances on the earth are constantly tending to arrive at a condition of greatest entropy, meaning "rundownness." Most of the metals, for instance, are oxidized to their most stable oxides and converted into other compounds which under existing conditions are extremely stable. Our ores are those stable oxides or salts. Although this condition has not been uniformly attained in the earth, while there are still, for example, natural deposits of metallic copper and silver, yet, unquestionably that is the direction in which the chemical changes are proceeding.

Now most of these substances, before they can be made use of, require certain chemical changes which are a reversal of the naturally occurring ones. The ores, oxides or salts of the metals, must be reduced to the elemental metals. This, of course, is the reversal of the processes occurring in nature, and to accomplish such a reversal work must be done, energy must be supplied.

If, then, the tendency is to attain the dead level—this state of equilibrium on our earth—what are the agencies or sources of energy that counteract this tendency and make possible the reverse reaction, the pumping of water up-hill, as it were?

In searching for such possible sources of energy which might serve this purpose, we find that a little heat is probably given to the surface of the earth from the interior, another very small amount is the result of certain radioactive chemical changes, the action of the tides contributes some, and a further amount is received from radiation from the stars and moon. But these amounts are quite inadequate and insignificant when compared with the primal source of our energy, the sun. The radiations from the sun constitute our main source of energy. This is our main and most consequential import, the only potent factor which counteracts the tendency of complete running down. It is important not only in such reactions as the smelting of ores, but equally to the life on the planet.

All living things on the earth demand for their maintenance and propagation a continuous supply of energy. The immediate source of this energy for living things is derived from food. All animals, including man, are fundamentally dependent upon plants for their food. Just as the herbivorous land animals are the source of food of the carnivorae, the diatoms are the fundamental source of food of the sea. The object of agriculture is essentially to provide man with such materials from which he is able to derive the energy necessary for the maintenance of his bodily activities, his growth and propagation.

MEANING OF "PHOTOSYNTHESIS"

So far as the composition of food material is concerned, there exists a closed cycle. Man feeds on animals, and animals on plants; the plants feed on the carbon dioxide given to the air by the animals as a result of the latter's use of food. Thus the plant reconverts the waste products of animal metabolism into food. The latter process is called *photosynthesis*. The plant absorbs through its leaves the carbon dioxide which is universally present in the atmosphere, and which is formed by the burning of coal, fuel oil, etc., and is also exhaled by animals. By means of the light from the sun the carbon dioxide thus absorbed by the leaves is changed into material such as sugar or wood, which can again

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[1] Received October 19, 1922.

be used as food for animals or as fuel. The net result, as far as the changes of materials are concerned in this interrelation of plants and animals, is *nil*. Thus, in brief, a plant yields a certain amount of substance which can be used as food. The food is consumed by man and thus enables him to do some work. Thereby the food material is burned in the body and is exhaled as the gas, carbon dioxide. Or the fuel is burned and the products of combustion escape into the atmosphere.

The fundamentally important point is in relation to the energy changes. The energy expended by the man has been permanently lost to a large extent; similarly, that obtained from fuel. The reconversion of the carbon dioxide into food or fuel material can be accomplished only by the use of a great deal of energy. The cycle is made possible only by the introduction of energy from without. This energy is derived from the sunlight, which the plant, unlike the animal, is able to utilize and convert the waste carbon dioxide again into food or fuel material.

It thus becomes evident that all life on the planet depends upon the energy derived from the sun through the intermediary of the plant—i. e., through the process of photosynthesis. Mankind lives entirely on the energy derived from the sun through the pursuits of agriculture.

Waste of Solar Energy

But in addition to this, we are squandering the principal of an enormous legacy of solar energy accumulated during the past ages. The plants, which alone are capable of utilizing the enormous floods of solar energy pouring upon the earth, have been at work for many ages prior to man's appearance upon the earth and have, during time which would make the total span of human history appear as but a moment, built the foundations upon which all his present eminence rests. This fossil vegetation, preserved as coal and oil, represents a very small fraction of the energy which has been falling on the earth and which has been conserved for man. It is kindled, its energy liberated and used in a thousand ways, and the rays of sunlight stored beneath the earth for millions of years give birth to a civilization such as the world has never known. It is this source of energy which has made possible the habitation of the temperate zones to the present extent, and on it depend our various modes of rapid transportation and our multifarious industrial activity. What may be called fossil solar energy, coal, made possible the reversal of the natural course by the smelting of ores for the production of metals. In fact, it is solar energy which counteracts the tendency of our earth to attain its maximum entropy.

But this great civilization of coal and steel is at the same time a most squandrous and profligate one; it is using the principal of its legacy in numberless new ways. Modern man's greatness depends upon his being essentially a tool-using animal. To increase the efficiency of one-man power has been his object for centuries. It is the power-driven machine that has done most of his work. But the source of energy which drives these machines is not a steady stream, it is being drawn from the accumulation of centuries. A year's consumption of coal at the present rate represents the accumulation of hundreds of years. The power of man to do work, physical work, the unit one-man power, is now an almost insignificant factor. A return to such a physical standard would almost certainly follow the failure of such sources of energy as man now has at his disposal. The quest of these sources of energy, coal and oil, is at present being pushed with a feverish intensity that has never been known before, and the competition for the possession of these stores recognizes no principles. The destiny of civilization is guided by and reflects the amount of available energy. When coal and oil are exhausted, the daily ration of solar energy will represent almost the entire means of livelihood; our mushroom civilization must pass like the historic empires of the past and we may expect the reappearance in the world once more of galley slaves and serfs.

Energy Resources Available

And thus the scientific world is awakening to the necessity of taking stock of our available resources of energy. Repeatedly, attention has been called to the inexhaustible floods of solar energy. With cool theoretical nonchalance the untold possibilities of the use of the sun's energy are constantly called to our attention. Yet, the chlorophyllous plant still remains the only converter of solar energy!

The student of photosynthesis cannot, even if he would, escape the practical applications of the problem. It is largely due to the fact that photosynthesis has been dealt with in an academic manner that its fundamental significance has until very recently not been more generally recognized and it has not been possible to enlist the interest and coöperation of workers in the allied sciences. To anyone who has been actively engaged in the investigation of this problem, it must be evident that progress toward its solution would be enormously accelerated by coöperative efforts from different angles.

Recently, interest in the subject has been very greatly stimulated through the realization on the part of industrial scientists that our available supplies of energy are being rapidly depleted.

Our main source of energy is coal, and although it is less than one hundred years since it has been put to extensive use as fuel, the present annual consumption is stupendous—about 650,000,000 tons. Each decade has brought a decided increase in the rate of consumption. While there are, of course, still enormous supplies to draw upon which, considered superficially, might allay all concern, our engineers, most qualified to judge, have repeatedly called attention to the necessity of preparedness on the fuel situation.

A far more serious situation is presented by the petroleum supply. The rapid development of internal-combustion engines of various types has brought about a tremendous demand for liquid fuel. This has increased at such a rate that it can be conservatively stated that the depletion of the petroleum supply in the United States is clearly in sight. A report of the country's foremost oil geologists, under the auspices of the U. S. Geological Survey, states:

> The estimated reserves are enough to satisfy the present requirements of the United States for only twenty years, if the oil could be taken out of the ground as fast as it is wanted.
>
> Individual wells will yield oil for more than a quarter of a century, and some of the wells will not have been drilled in 1950. In short, the oil cannot all be discovered, much less taken from the earth, in twenty years. The United States is already absolutely dependent on foreign countries to eke out her own production, and if the foreign oil can be procured, this dependence is sure to grow greater and greater as our own fields wane, except as artificial petroleum may be produced by the distillation of oil shales and coals, or some substitute for petroleum may be discovered.

It is, therefore, not surprising that every available source of energy is being considered to meet the situation which is approaching.

Another very considerable source of energy is that developed from the water powers. Theoretically, this is virtually an inexhaustible supply and one of relatively high efficiency. Mr. Charles P. Steinmitz[2] has calculated on the basis of collecting every raindrop which falls in the United States and all the power it could produce on its way to the ocean being developed, that there would be possible about three hundred million horse power. This enormous figure represents about the amount received from our present total consumption of coal. Thus, this theoretical hydroelectric power would just about cover our present coal consumption, but leave nothing for future increased needs or to cover other sources of energy now in use. Moreover, this figure for hydroelectric power is purely hypothetical, of which only a small fraction represents that actually available, which, when united with other difficulties such as equipment and limitations of distribution, shows very clearly that all the water powers of the country cannot suffice.

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[2] "The White Revolution," *Survey Graphic*, 1 (1922), 1035.

The question of liquid fuel is of particular importance in this consideration. The great success of the internal-combustion engines in the automobiles, airplanes, tractors, etc., as well as the many uses of the Diesel engine, has very greatly influenced our economic life, and, as has been stated, it is soon to exhaust our natural resources of liquid fuel. Much attention has, therefore, been given to the production of liquid fuel other than petroleum. Thus far, the investigations along these lines have almost universally led to the opinion that the substance best suited to these needs is alcohol. This is on the basis that alcohol can be produced from vegetable material and is the most direct route from solar energy. It is thus proposed to develop a photosynthetic industry on the basis of agriculture, the products of which are to be converted into alcohol by means of fermentation.

This is, of course, the practical end of the photosynthesis problem. There are so many factors which come into consideration on careful study of the problem in its broadest application, that it is not surprising that some of the most important of these have been entirely disregarded or not given the attention they deserve.

Possibilities of Photosynthesis

In considering the sun as a source of energy, two possibilities suggest themselves. The first is a direct utilization of solar energy through some device by means of which the energy could be transformed and stored; the other is by means of the natural process of photosynthesis. Disregarding as inadequate those arrangements that transform solar energy into heat and attempt to use boilers of various kinds, no advance has been made in the direct utilization of solar energy. A transformation of the energy based upon chemical methods has received little attention. The reason for this is that such known photochemical reactions as are endothermal—that is, processes in which energy is stored—are not of a nature to encourage development. The process of photosynthesis in the green plant is such a transformation and storing of energy. Nature has worked out this problem and has done it in a most remarkable manner.

We are therefore still centering our speculations on the plant as a transformer of energy through the production of carbohydrate material. With complete disregard of biological facts, chemists have continued to develop schemes for the employment of the photosynthetic process and to evolve theories of the chemistry of photosynthesis. One of the fundamental fallacies in these speculations may be indicated by a quotation from a recent technical article: "Photosynthesis is simply a manufacture that provides material used in the process of living." It is falsely conceived that this process of manufacture is not a function of the living plant.

There have also been many erroneous and misleading statements regarding the amount of energy radiated from the sun which reaches the surface of the earth. In nearly all the technical discussions on this subject that have appeared recently the calculations are based upon the value of 3 calories per square centimeter per minute. Now this value does not represent the amount of energy which reaches the earth. It is the old value of the solar constant—i. e., the amount of solar energy at the outside of the earth's atmosphere.

The true value of this solar constant is still a subject of some dispute, and it is, in fact, of secondary interest to the immediate problem of the utilization of solar energy on the earth. A great many determinations of the amount of energy received on the earth have been made, and it is certain that a very considerable amount of solar radiation is absorbed in the atmosphere of the earth. For the present purpose, the intensity of solar radiation reaching the earth can be placed at 1.5 calories per square centimeter per minute. On this basis we would receive 5400 large calories per square meter during six hours. Now one kilogram of coal when burned develops about 8000 large calories; so that six hours of insolation per square meter represents a heat equivalent of 0.675 kilogram of coal, and on an acre, 16.41 tons of coal. This for ninety days of insolation would equal 1476.63 tons.

In order to gain some idea of the degree of efficiency of the photosynthetic process in utilizing solar radiation as expressed in the yield of agricultural products, the heat value of a cereal crop can serve as a comparison. Taking the very large yield of 50 bushels, or 17.619 hectoliters of wheat per acre, and considering this as entirely starch, we get an energy equivalent of 0.623 ton of coal. This last figure of about two-thirds of a ton of coal is to be compared to the 1476 tons, representing the total solar radiation during a period of ninety days, approximately a growing season.

This, then, is the amount of solar energy received at the surface of the earth, and in a practical sense, the amount of this energy that is stored by means of agriculture. It is a very striking fact that the processes of organic nature are exceedingly inefficient and wasteful. This, of course, is so of necessity. Faced with the uncertainties of environmental and climatic conditions, only such processes as are allowed a wide margin of safety are assured the living organism of survival. These figures also indicate that agriculture, as the only photochemical industry, is utilizing but a very small portion of the available energy.

In discussing the possibility of preparing liquid fuel from grain, Boyd[3] makes the following statements:

> The large amount of motor fuel required seems to exclude the possibility of preparing any considerable percentage of the necessary amount from foodstuffs. In illustration of this statement the following figures are of interest:

	Bushels
Average annual U. S. production of corn 1913–1919	2,740,000,000
Average annual acreage in corn 1913–1919............	160,000,000
Alcohol from the corn at 2.75 gallons per bushel.......	7,500,000,00

> The heating value of this amount of alcohol is about equal to that of 5,000,000,000 gal. of gasoline. The production of gasoline in the U. S. during 1920 was very close to this amount, about 4,900,000,000 gal. The average acreage in corn as given above is equal to 166,000 sq. mi., which is more than four times the total area of Ohio. In view of the fact that the possible alcohol production from corn represents close to 60 per cent of the total possible amount of alcohol that could be prepared from all of the starch and sugar containing foodstuffs produced in the United States, and that such a large acreage is required for its production, the possibility of a sufficiently large increase in production of such materials to be diverted to the manufacture of motor fuel seems very unlikely. At any rate, if large quantities of motor fuel are to be prepared from vegetation, another material, if not instead of foodstuffs at least in addition to foodstuffs, must be relied upon as a source.

It seems highly questionable whether the use of the products of photosynthesis offers a rational solution to the problem of industrial energy. It must be borne in mind that the products of photosynthesis are essential to human life as the fundamental source of food. The trend of modern investigation of the chemical, as well as the economic phases of the food problem, strongly supports the dictum that agriculture will always be the basis of food production and that this cannot be supplanted by any artificial method. The materials which are elaborated by plants are directly essential to the well-being of man. Furthermore, any serious disturbance in the way of diverting agricultural products from their use as food to industrial ends would undoubtedly be fraught with profound economic disturbances.

Cellulose as Source of Fuel

There is one other plant product about which there has been much speculation regarding the possibilities as a source of liquid fuel; that is cellulose. There are so many factors which enter into a rational consideration of the possibilities of producing alcohol from cellulose that no adequate analysis of the problem has as yet been attained. These factors embody the biological aspects, the chemical methods, and the economic possibilities. It cannot be claimed that any one of the many compilations and discourses offered since the great interest in this subject has arisen, treat adequately the complexities of the problem. Briefly, the points that demand consideration are the availability of cellulose material in sufficient quantity and the continuous supply thereof, an exact and broad knowledge relative to the chemical processes of converting cellulose to alcohol, and the cost of raw material, manufacture, and transportation, as well as the complexities of labor and influence on other industries. In different sections of the country where different kinds of wood come into consideration there are problems peculiar to each locality.

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[3] "Motor Fuel from Vegetation," This Journal, **13** (1922), 836.

Much of the speculation as to the use of cellulose for conversion into alcohol is based upon the utilization of waste material in the forests and at the mills. Of the twenty-six billion cubic feet of wood cut annually, the major portion represents accumulated virgin timber, so that this source cannot be considered as a permanent one. To what extent and how soon the depletion of virgin forests will be met by intensive forestry, is a practical question that seems difficult to answer.

These considerations also obtain for the frequently repeated statements of the use of humid tropical regions for growing material from which alcohol could be manufactured. It must be borne in mind that for any such undertaking reliance could not be placed upon extant material, recourse would have to be taken to very extensive cultivation. Moreover, such an undertaking must not interfere with the area now used for the production of foodstuffs.

COMPLEX NATURE OF AGRICULTURAL INDUSTRY

Finally, in advocating the natural photosynthetic process through agricultural industry as the producer of a supply of energy there has been evidenced great neglect of the fact that agriculture is a highly sensitive and complex industry. The fact seems to be too readily forgotten that agriculture deals with biological processes, that solar radiation is but one of many factors influencing the developments of plants, and that in almost every place on the earth where agriculture might be undertaken there is far more light than the plant is capable of utilizing.

The uncertainties of agricultural industry arise from the very complex nature of the biological processes and balances involved in the development of a growing organism. Not only the multiplicity of pests and diseases with which agricultural endeavor must contend, but the relatively sensitive adjustment to climatic environment increases the hazards of this industry enormously. Thus, of course, the growth of plants is not dependent on light only, but on a variety of factors not associated with solar radiation.

The fact that during critical periods in the development of a plant slight changes in climatic conditions during a short time may greatly reduce or entirely destroy a crop, serves to emphasize the hazard of obtaining energy through the intermediary of plants. In agriculture, water supply and temperature are far more variable and determining factors than light intensity. On the proper coördination of these two factors, probably more than any other, depends the success of crop production.

On the other hand, considering alone the solar energy which it is our object to store, there falls on the earth during most of the year a great deal more than any plant is capable of utilizing.

SOLUTION OF THE PROBLEM

Nature has worked out a method of utilizing solar energy. It is the duty of the scientist to learn the precise manner in which this is accomplished. He need not be timid about competing with nature. He has many cases to his credit of surpassing the processes of nature both in efficiency and reliability. There are many substances now effectively produced artificially which were formerly obtainable only from plants or animals. It is true that in the utilization of radiant energy there are a great many intricate difficulties to be overcome, but to anyone who has given the problem thorough study it must be evident that we are already in possession of much knowledge which can find immediate application to this problem. As the basis of agriculture, the problem of photosynthesis needs development and clarification. As the only known photochemical reaction, proceeding in the visible spectrum, in which there is a large increase in the potential energy of the products, photosynthesis serves as a guide to the utilization of solar energy. Although the chemical reactions constituting the photosynthetic process are of a highly complex and intricate nature, sufficient investigation has been done to justify the conclusion that the problem is amenable to physico-chemical treatment. However, no single academic division of science, such as botany, chemistry, or physics, is of itself sufficiently rich in concepts and methods to attack the problem adequately. The most promising outlook for success in this field would be offered through an organization by which information from the various allied fields can be collected and focused on the chemical and energy changes taking place in the process of photosynthesis. In view of the present academic division of the sciences and the variety of special training which is requisite for such an undertaking, coöperative effort offers the only rational method of advance.

Photosynthesis is essentially a problem of energy transfer. Those aspects of the problem involving the changes of material, the rates of these changes, and the conditions under which they occur, require the methods and conceptions of organic chemistry and physiology. In order to determine the kinetics of these same reactions and the mode of energy transfer, a very different method of experimentation is required. These latter lead directly to the fundamental problems of radiochemistry and require the most advanced methods of physical experimentation.

Has not science here a unique opportunity to lead the way in real coöperation and to demonstrate its true democratic value?

The embryo of a seed, during its first days after sprouting, lives upon material stored for it by the parent, until it gains strength and becomes an independent plant. Throughout nature the young are nurtured and protected until they can care for themselves. So man has had his great patrimony of fuel to help him in his first faltering steps to dominion over his environment. As he grows in intellectual stature, he must meet the problem of physical necessity, a problem of energy pure and simple, ere he can aspire to true independence. The great contribution of the nineteenth century was the establishment of the doctrines of energy. To the twentieth falls the task of freeing us from our economic placenta.

Research on Liquid Carbon Dioxide

The Liquid Carbonic Division of the Compressed Gas Manufacturers' Association announces the establishment of an Industrial Fellowship in the Mellon Institute of Industrial Research of the University of Pittsburgh, for the purpose of classifying, studying, and developing the uses for liquid carbon dioxide. The founding of this fellowship is in accord with the desire of the members of the association to coöperate with users and prospective users of liquid carbon dioxide, with the object of developing efficient means of applying the gas and of obtaining fundamental data bearing on its use in various industries.

In addition to conducting research work, the fellowship will be made a clearing house of information regarding various uses of liquid carbon dioxide, and data will be kept on file for the accommodation of prospective users of this product.

The present incumbent of the Industrial Fellowship is Charles L. Jones, who will be glad to correspond with anyone interested in the use of liquid carbon dioxide in industry.

Progress toward the Artificial Synthesis of Carbohydrates and Proteins[1]

By R. W. Thatcher

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While it is not within the lifetime of the present generation that the practices of civilized men will result in critical depletion of the stored energy of the plants of the Carboniferous Era and of the mighty primeval forests of the newly discovered countries of the earth, already there are indications of the approach of that unfortunate time. Before long, as time is counted in history, necessity will compel serious consideration of the problem of replenishment or substitution for the energy stored in plants to supply the needs of mankind. Even now there are signs of approaching difficulties. The demand for foodstuffs for increasing populations, while temporarily halted by the depopulation of the World War and subsequent starvation, will begin anew within a very few years. The inroads of modern necessities upon our rapidly diminishing supplies of timber, and the ravages of insect pests and plant diseases upon economic food and fiber crops, stimulate serious, sober thought in the minds of those who are following the evolutionary development of the earth's inhabitants. The contemplation of the approach of the time when the last ton of coal shall be mined and the last gallon of mineral oil consumed gives to the thoughtful student the same blood-chilling sensation that affects him when he sees through his powerful telescope the cold and barren wastes of the moon.

While these present indications of future dire necessities are not sufficient to cause general gloomy forebodings, they furnish an adequate reason for the utmost interest by chemists in the possibility of a better understanding of how nature has through countless ages stored up the vast reservoirs of solar energy which modern civilization is now so rapidly dissipating. Photosynthesis has come to have an intensely practical, as well as a fascinating theoretical, interest.

Recent Discoveries

During very recent years certain biochemists have devoted much study to this problem, and, while it is far from being solved, some of its aspects are better understood than they were even five years ago. Exactly how the plant cell accomplishes its total constructive function is as yet a mystery, but some of the steps in the process are now understood and have been artificially duplicated. Several decades ago Emil Fischer and his students accomplished the artificial synthesis of many soluble sugars and of certain polypeptides which closely resemble the natural proteins, but by roundabout processes, and by means of violent chemical reagents, such as could not possibly be conceived to be in any way analogous to those which a plant cell utilizes in its synthetic work. For this plant process it has long been recognized that the gases of the atmosphere are the real initial raw products, and certain fairly simple empirical chemical equations have been cited as representing the steps through which the photosynthetic process goes on; but until very recently attempts to duplicate experimentally and under artificial conditions any of these simple transformations have always failed. Furthermore, while it has been accepted as a fact that chlorophyll-containing plant cells are able to synthesize carbohydrates of all degrees of complexity from the atmospheric gases, until within the past five years it has been supposed that, although the gaseous nitrogen of the air is undoubtedly the ultimate source of supply of this element, the synthesis of proteins by plants requires the fixation of combined nitrogen in the soil prior to its absorption by the roots of higher plants.

Very recently, however, Benjamin Moore and his associates[2] have demonstrated that unicellular algae, in the absence of all nitrogen except that in the atmosphere and in the presence of carbon dioxide, can fix nitrogen and grow and form proteins by a process which derives its energy solely from light and is, therefore, photosynthetic. They found also that the rate of this unicellular growth may be accelerated by the presence of oxides of nitrogen such as are present in the atmosphere. Further, Moore has concluded from other experiments[3] that green seaweed can and does grow and synthesize both carbohydrates and protein, using only the carbon from bicarbonates of calcium and magnesium present in sea-water and nitrogen from the atmosphere. He explains the failure of fresh water and terrestrial plants to accomplish the same transformations as being due to their inability to establish a satisfactory exchange of alkali material between themselves and their enveloping medium, as do the sea plants.

Photosynthesis of Carbohydrates

As to the mechanism by which photosynthesis of carbohydrates is accomplished, recent investigations[4] indicate that under the stimulus of short wave length of light (200 $\mu\mu$) aqueous carbon dioxide can be fairly easily converted into formaldehyde, without the presence of chlorophyll or any other energy-absorbing agent; and that this photosynthesis can be actively photocatalyzed by certain basic colored substances, such as colloidal uranium hydroxide, ferric hydroxide, methyl orange, or malachite green, in the presence of visible light. They also point out that the polymerization of formaldehyde into reducing sugars takes place easily in the presence of light of wave length 290 $\mu\mu$ and that this polymerization can likewise be photocatalyzed by deeply colored alkaline copper solutions. These reactions have been shown to be reversible, depending upon the type of light used and the character of the photocatalyst which is present in the reacting mixtures. Thus, in a system containing reducing sugars, formaldehyde, carbon dioxide, and water, equilibrium is set up between these various components at various points depending on the wave length of the light which falls on the mixture and the nature of the photocatalyst which is present. If ultraviolet light of very short wave length is employed, equilibrium lies far over on the carbon dioxide side; in the presence of a suitable photocatalyst to absorb light of slightly greater wave lengths, formaldehyde is produced in considerable quantities; while in the presence of photocatalysts which absorbs light of wave length 290 $\mu\mu$, active polymerization of formaldehyde to reducing sugar goes on, and, in the presence of a photocatalyst which is capable of catalyzing both stages of the reaction, the equilibrium is shifted entirely over to the reducing sugar side. It has been suggested, although not yet experimentally demonstrated, that chlorophyll is an ideal photocatalyst for both stages of the synthesis of soluble sugars from carbon dioxide and water, and the formation of

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[1] Received July 24, 1922.

[2] *Proc. Roy. Soc.* (*London*), **91B** (1920), 201.

[3] *J. Chem. Soc.* (*London*), **119** (1921), 1555.

[4] *Ibid.*, **119** (1921), 1025.

carbohydrates in the growing leaf from very small concentrations of carbon dioxide without the existence of free formaldehyde as an intermediate product is thus explained. If this explanation is finally given successful experimental demonstration, the next step seems fairly obvious—namely, that the reversible changes of reducing sugars to more complex carbohydrates may be likewise photocatalyzed, presumably by light of still greater wave lengths. If this should be found to be true, the entire mechanism of the production of carbohydrates from carbon dioxide and water will be understood, and an ample supply of the photocatalytic chlorophyll, or other plant pigments for artificial synthesis of these important food substances, will be easily available in the noneconomic plants of the country. It would, therefore, seem that the possibility of economic artificial synthesis of one of the important constituents of human food is at least brought much nearer to realization by these recent biochemical researches.

As to the actual part which chlorophyll plays in the photosynthesis of carbohydrates, three possible modes of action are now receiving experimental study. The first of these, which has naturally been longest considered as the probable function of chlorophyll, is that it acts chemically as a catalyst by forming unstable intermediate products with formaldehyde or possibly other simple intermediate compounds of the photosynthetic process. Indeed, several investigators[6] have shown that chlorophyll actually does form a compound with formaldehyde from which complex the formaldehyde may be either given off or absorbed in order to establish a proper equilibrium in the photosynthetic process, and to afford in the plant a mechanism by which the quantity of free formaldehyde is regulated. In this way the amount present in free form at no time reaches that which would be toxic to the cell protoplasm. The second of these conceptions is that, regardless of the color and of the general chemical reactivity of chlorophyll, the mineral constituent (magnesium) which it contains is held in proper colloidal form to exert a definite catalytic effect upon the photosynthetic process. The third, and most recent, explanation of the mechanism of chlorophyll action is that the pigment acts as a photocatalyst, or light screen, to absorb and transmit the energy from light rays of the proper wave length to accomplish the several steps in the photosynthesis of carbohydrates.

As has been pointed out above, this last conception has very recently been given experimental confirmation, and the artificial synthesis of simple carbohydrates from atmospheric gases under the influence of proper photocatalysts has already been accomplished.

Photosynthesis of Proteins

Not as much progress toward an understanding of the mechanism of the synthesis of proteins by plants, or toward the successful artificial duplication of the process, has yet been made as has in the case of the carbohydrates. It has been shown that the ordinary synthesis of proteins by plants supplied with nitrogen in some oxidized (preferably nitrate) form is not necessarily a photosynthetic process, as it can occur in the dark and in the absence of chlorophyll or any other light-absorbing pigment. However, atmospheric nitrogen cannot be used by plants for this purpose, except in the case of certain bacteria, notably those which live in symbiosis with the legumes in the nodules on the roots of the host plants and other low plants, particularly marine algae. As has been pointed out, it has recently been suggested by Moore that the ability of green algae to synthesize proteins from atmospheric nitrogen, by a process which seems to be photosynthetic—i. e., deriving its energy from solar light—is apparently due to their favorable environment for free exchange of alkali material between their tissues and the surrounding medium, sea water. This indicates that the synthesis of proteins through the nitrogen→ammonia→amino acid→protein course may yet be understood and possibly artificially duplicated in the near future. Heretofore, it has been supposed that the oxidation of atmospheric nitrogen to nitrate form is a necessary preliminary step to its utilization in the synthesis of proteins, at least by ordinary cell protoplasm. Presumably, the nitrate nitrogen must then be reduced in the plant to nitrite, and then to the ammonia form, in order to enter the amino arrangement which is required for the greater proportion of the protein nitrogen. These preliminary oxidation and reduction changes have heretofore been little understood, but progress toward a satisfactory knowledge of the mechanism of their control is now being made. Artificial syntheses of amino acids by the action of ammonia upon glyoxylic acid and sorbic acid, both of which may be obtained by the oxidation of simple sugars, have been accomplished. The reversible condensation of these amino acids into proteins is readily accomplished in all living protoplasm under the influence of special enzymes which are almost universally present in the cytoplasm.

We are still in the dark as to the mechanism by which this condensation is brought about, but recent investigations have thrown so much light upon the whole photosynthetic process that it seems reasonable to expect that we may soon reach a working understanding of the condensation process, both of the sugar $\rightleftharpoons$ starch and of the amino acid $\rightleftharpoons$ protein transformations. When this result is reached, a long step will have been taken toward the solution of the problem of artificial synthesis of food products, with which to supplement the stored energy of bygone ages that is being so rapidly dissipated by the demands of our modern civilization.

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[6] *Proc. Roy. Soc. (London)*, **80B** (1908), 30; **82** (1910), 226.

Use of Oxygen in Metallurgical Operations

Use of oxygen in connection with the enrichment of the blast in the blast furnace and in practically all phases of pyro-metallurgical work will furnish the key to success in the further development of such metallurgical operations, according to Dr. F. G. Cottrell, formerly director and now consulting metallurgist of the United States Bureau of Mines, who first directed the Bureau's attention to this subject. Through this enrichment process it is hoped to increase the efficiency of metallurgical operation with a resultant production of metals at lower cost and possibly the use of lower grade ores.

The Bureau of Mines now has outlined plans for two studies which will be carried on simultaneously. The first will cover the present-day processes for the production of oxygen, in order to determine the feasibility of attempting to produce oxygen, or oxygenated air, in such amounts and at such a cost as to permit of its use in metallurgical operations. The second study will be devoted to the feasibility of using oxygen, or oxygenated air, in metallurgical operations.

Because of his interest in this investigation, M. H. Roberts, vice president of the Franklin Railway Supply Co., was asked to select an advisory committee to work with the Bureau of Mines and to act as chairman of this committee. The committee will consist of F. G. Cottrell, director of the Fixed Nitrogen Research Laboratory; W. L. DeBaufre, chairman of the mechanical engineering department of the University of Nebraska; D. A. Lyon, chief metallurgist of the Bureau of Mines; R. B. Moore, chief chemist of the Bureau of Mines; R. C. Tolman, professor of physical chemistry and mathematical physics, California Institute of Technology; J. W. Davis, mechanical engineer of the Bureau of Mines; F. W. Davis, metallurgist of the Bureau of Mines; Frank Hodson, president of the Electric Furnace Construction Company; and P. H. Royster, assistant metallurgist of the Bureau of Mines.

Previous to the war, some work was done in Belgium on the enrichment of the blast with oxygen in connection with the smelting of iron ores in the blast furnace. In the United States, the late J. E. Johnson, Jr., was interested in the possible use of oxygen in metallurgical operations and carried on some experimental work along these lines previous to his death.

On November 3, 1922, Dr. Edgar F. Smith delivered a lecture on Joseph Priestley before the Priestley Club of the University of Pennsylvania. On this occasion various Priestleyana were for the first time exhibited to the public.

Manuscript Bibliographies in Chemistry and Chemical Technology

Compiled by Clarence J. West and Callie Hull

Research Information Service, National Research Council, Washington, D. C.

(Concluded)

Graphite:

H. G. Ferguson, U. S. Geological Survey, Washington, D. C. Entries by author, subject, and locality. Abstracts included in part. Complete to 1919.

See also Refractories (Schurecht).

Grignard Reaction:

C. W. Porter, University of California, Berkeley, Calif. 500 entries. 1900–1921. Many important contributions and some of no value.

Gypsum:

Frank A. Wilder, North Holston, Va. 600 entries by author, title, and subject. Four-fifths complete. To be published in monograph of Iowa Geological Survey.

Heat Transmission:

Heat transmission: evaporating and heating apparatus. W. L Badger, University of Michigan, Ann Arbor, Mich. 2000 entries, by author and subject. 1850–date. Abstracts included. 25 per cent complete.

Heating Apparatus:

See Heat Transmission (Badger).

Heterogeneous Equilibria:

E. C. McKelvy and L. Yurow. Thousands of entries, by author and subject. Up to 1919. Abstracts and critical comments in many cases. Much data tabulated and plotted. Incomplete, especially for later years. For consultation, write Bureau of Standards, Washington, D. C.

Hydrocyanic Acid:

See Insecticides and Fungicides.

Hydrogen:

Low temperature research; liquefaction of hydrogen and properties of liquid hydrogen. J. C. McLennan, University of Toronto, Toronto, Canada. 1898–1920. Some abstracts included.

Hydrogenation of Oils:

Charles Baskerville Incomplete. For consultation, write Library, College of the City of New York, New York, N. Y.

Hydrotherapy:

Influence of bathing on metabolism. H. A. Mattill, University of Rochester, Rochester, N. Y. 200 entries, by author. 1890–date. Abstracts usually included. Probably all the important contributions.

Industrial Chemistry:

Industrial inorganic, organic, electro, and combustion chemistry. R. K. Strong, Reed College, Portland, Ore. Entries by subject. 1896–date.

Inorganic Chemistry:

See Industrial Chemistry (Strong).

Insecticides and Fungicides:

J. J. Davis, Purdue University, Lafayette, Ind. 4000 or more entries by subject. 1860–date. Abstracts included in some cases. Fairly complete

Chemical composition of proprietary insecticides and fungicides and chemical composition and disinfectant action of proprietary disinfectants. J. K. Haywood, Insecticide and Fungicide Board, U. S. Department of Agriculture, Washington, D. C. 9500 entries, by subject. 1910–date. 90 to 95 per cent complete. Cannot be consulted or duplicated, but information will be given state and government scientists in exceptional cases, on understanding that results will not be made public.

Fumigation with hydrocyanic acid gas. E. R. Sasscer and R. S. Woglum. Entries by author. Very complete up to 1920. Abstracts included in a few cases. For consultation, write E. R. Sasscer, Federal Horticultural Board, Washington, D. C.

Lime sulfur as a spray. V. I. Safro. 612 entries, by author. Earliest references up to and including 1911. Abstracts included. Very complete. For consultation, write Department of Entomology, Oregon Agricultural College, Corvallis, Ore.

Miscible oil sprays in combination with other spray materials. Leroy Childs, Hood River, Ore. Well started.

Organic insecticides and fungicides, including hydrocyanic acid, chloropicrin, and others. Clarence J. West, National Research Council, Washington, D. C. 300 entries, by author. Three-fourths complete.

See also Lead Arsenate (Dickey), Poisons (Gray).

Iron:

Effects of sulfur and phosphorus on the properties of iron and steel. 350 entries, by author (35 typewritten pages). For consultation, write joint committee on phosphorus and sulfur in steel, attention of H. L. Whittemore, Bureau of Standards, Washington, D. C.

Iron ores. R. J. Holden, Virginia Polytechnic Institute, Blacksburg, Va. To be published by the Virginia Geological Survey.

Iron ores of the United States. E. C. Harder, 1111 Harrison Bldg., Philadelphia Pa. Entries by author and locality. Moderately complete to 1919, inclusive.

Malleable cast iron. E. S. Davenport. 38 entries, by author. 1914–1922. For consultation, write Eastern Malleable Iron Co., Naugatuck, Conn.

Malleable iron. A. E. White, University of Michigan, Ann Arbor, Mich. 83 entries. 1910–1921. Includes most of the pertinent books and articles bearing on the subject.

See also Lead Coatings (Berolzheimer).

Kapok:

Arthur D. Little, Inc., Cambridge, Mass. 22 entries, by author.

Kauri Gum:

Arthur D. Little, Inc., Cambridge, Mass. 14 entries, by author.

Lactose:

Lactose (milk sugar): scientific and industrial. Harper F. Zoller, 3345 Grand River Ave., Detroit, Mich. 44 entries. Up to 1922.

Lead Arsenate:

Corona Chemical Division, Pittsburgh Plate Glass Co., Milwaukee, Wis. 80 entries, by author, title, and subject. 1819–1916. A few abstracts included. 85 per cent complete. For consultation, write C. B. Dickey, Superintendent.

Lead Coatings:

Lead coatings on iron and steel. D. D. Berolzheimer. Entries by author and title. 1904–1914. Thorough for years covered, including a few older references. For consultation, write National Lead Co., 129 York St., Brooklyn, N. Y.

Leather:

Leather and tanning chemistry, tanning materials, etc. J. S. Rogers, Morgantown, N. C. 300–400 entries. 1909–1917. Abstracts included in some cases. Not very complete.

Light:

See Photochemistry.

Lime:

The uses of lime. M. E. Holmes, 918 G St., N. W., Washington, D. C. Several hundred entries, by subject. 1920–date. Very brief abstracts included. Complete.

Low Temperature Carbonization:

The Barrett Co., 40 Rector St., New York, N. Y. 154 entries, by author, subject, and patents. 1873–date. Abstracts included.

Carbonization of coal, particularly low temperature carbonization. Roland P. Soule. 300–400 entries, by subject. 1860–1922. Abstracts included. Very complete on low temperature carbonization and theories of carbonization. For consultation, write Prof. J. J. Morgan, Havemeyer Hall, Columbia University, New York, N. Y.

Lubricating Oils:

See Petroleum (Smith).

Magnesite:

See Refractories (Schurecht).

Maltose:

Maltose in acid-hydrolyzed starch products. L. F. Hoyt, Larkin Co., Inc., Buffalo, N. Y. 66 entries, by author, title, and subject. 1812–1913. Complete as facilities permit.

Marine Borers:

See Wood Preservation (West).

Meat:

Dried meat. Arthur D. Little, Inc., Cambridge, Mass. 22 entries, by author.

Meat packing industry. Library of Congress, Washington, D. C. 150 entries, by author. Up to 1920.

See also Flesh.

Mesothorium:

Herman Schlundt, 303 Hicks Ave., Columbia, Mo. 55 entries, by author. 1907–1920. 85 per cent complete.

Metabolism:

Animal nutrition, calorimetry. H. F. Armsby, State College, Pa. 12,177 entries, by subject mostly, many by author and title. 1870–1922. Abstracts included. Very complete in references to plants—culture, fertilizer, etc., field crops; general science—animal physiology, metabolism; foods, animal—nutritive value, animal products.

Carbohydrate metabolism and physics and chemistry of the blood. E. L. Scott, 437 W. 59th St., New York, N. Y. 3500 entries, by title and subject. From earliest literature to date. Abstracts included in about 50 per cent. 25 per cent complete.

Digestion and assimilation of fat; digestion, fasting, and pathological lipaemia. S. H. Gage, Stimson Hall, Ithaca, N. Y.

Fate of foreign organic compounds in the animal body, and synthesis of amino acids in the body. Carl P. Sherwin, Fordham University, New York, N. Y. 2000 entries. 1912–date.

Influence of mineral waters on metabolism. H. A. Mattill, University of Rochester, Rochester, N. Y. 150 entries, by author. 1890–date. Abstracts usually included. All important contributions.

Metabolism of chickens and nutritive requirements. H. A. Mattill, University of Rochester, Rochester, N. Y. 200 entries, by author. 1890–date. Abstracts included in about one-half the entries. 75 per cent complete.

Metabolism of mineral matter. H. A. Mattill, University of Rochester, Rochester, N. Y. 600 entries, by subject. 1906–date. Abstracts usually included. 90 per cent complete.

Nutrition. J. F. McClendon, 815 Fulton St., S. E., Minneapolis, Minn. More than 1000 entries, by subject. 1918–date. Abstracts included.

Nutrition, bread, and allied topics. C. E. Halstead, Ward Baking Co., New York, N. Y. Entries by author and subject. 1850–date. Abstracts frequently included. 90 per cent complete.

Protein storage in protoplasmic tissue. W. S. Ritchie. Entries by author and title. 1898–1922. Rather complete. For consultation, write C. R. Moulton, 105 Schweitzer Hall, Columbia, Mo.

See also **Cholesterol** (Arnold); **Hydrotherapy** (Mattill); **Proteins** (Mattill).

Metallurgy:

Mining, metallurgy, geology. H. O. Hofman, Massachusetts Institute of Technology, Cambridge, Mass. Hundreds of entries, by author. 1885–1920. All leading articles in periodicals.

Methanol:

Charles Baskerville. Incomplete. For consultation, write Library, College of the City of New York, New York, N. Y.

Mildewproofing:

See **Waterproofing** (Fenn).

Milk Secretion:

Biochemistry of milk secretion and related nutritional topics. Edward B. Meigs, Dairy Division, Experiment Station, Beltsville, Md. 550 entries, by author. 1850–date. A few abstracts included. No attempt at completeness.

Mineral Matter:

See **Metabolism** (Mattill).

Mineral Waters:

See **Metabolism** (Mattill).

Motor Fuels:

Motor fuels and petroleum. E. H. Leslie, University of Michigan, Ann Arbor, Mich. Several thousand entries, by author and subject. Up to date. Abstracts included on many of the cards. Literature and patents are covered thoroughly.

See also **Alcohol** (Leslie).

Naphthalene:

Homologs of naphthalene. The Barrett Co., 40 Rector St., New York, N. Y. 142 entries, by author and subject. 1869–date. Abstracts included.

Naval Stores:

Naval stores (turpentine and rosin). A. W. Schorger. 5000 entries (572 typewritten pages) by author and subject. Up to 1912. Abstracts included. Every available article read and abstracted. Important articles translated or long abstracts made and deposited in files, with file number given in the bibliography. For consultation write Forest Products Laboratory, Madison, Wis.

Nitric Acid:

See **Nitrogen Fixation** (Zeisberg).

***p*-Nitrobenzaldehyde:**

C. G. King. 1860–1920. Entries by author and names of compounds. American, English, and German abstract journals covered. For consultation, write Library, University of Pittsburgh, Pittsburgh, Pa.

Nitrogen Fixation:

American Cyanamid Co., 511 Fifth Ave., New York, N. Y. Not complete.

Nitrogen fixation, nitric acid manufacturing, nitric acid concentration. Fred C. Zeisberg, E. I. du Pont de Nemours & Company, Wilmington, Del. 1500 entries, by subject. Abstracts included. All U. S. patents and a number of literature references. 75 per cent complete.

Production of synthetic nitric acid and synthetic ammonia. Engineering Societies Library, New York, N. Y. 847 entries. 1788–1917. Abstracts included.

Nitro-*o*-phthalic Acid:

See **Phthalic Acid** (Bogert).

Nutrition:

See **Metabolism; Proteins** (Mattill).

Occupational Diseases:

Occupational diseases in chemical trades. Charles Baskerville. Incomplete. For consultation write Library, College of the City of New York, New York, N. Y.

Oil(s):

See **Fats and Oils, Castor Oil, Hydrogenation, Viscosity, Oil Shale, Wood-tar.**

Oil Shale:

Oil shale and shale oil. R. H. McKee, E. E. Lyder, and R. T. Goodwin, Department of Chemical Engineering, Columbia University, New York, N. Y. 450 entries, by authors. 1825–July 1921. Abstracts included. Complete as possible. Will appear in AMERICAN CHEMICAL SOCIETY monograph on this subject.

Oil shales. Eliot Blackwelder, 317 Railway Exchange Bldg., Denver, Colo. 125 entries, by author and title. Abstracts in many cases. 60 per cent complete.

Oil Sprays:

See **Insecticides and Fungicides** (Childs).

Optical Isomerism:

Roy B. Davis, University of the South, Sewanee, Tenn. 2500 entries, by author and subject. Up to 1917.

Organic Chemistry:

See **Grignard Reaction** (Porter); **Industrial Chemistry** (Strong); **Names of Organic Compounds.**

Paper:

See **Pulp and Paper** (Libby), (West).

Petroleum:

Emulsions in petroleum (lubricating oils). Harrison P. Smith, 615 South Virgil Ave., Los Angeles, Calif. 35 entries, by author and subject. Up to 1920. Abstracts included. Not very complete.

Geology and statistics of petroleum for the United States. G. B. Richardson, U. S. Geological Survey, Washington, D. C. Several hundred entries, by locality. The most important publications since 1900.

Latin-American petroleum. E. W. Shaw, 302 Cosden Bldg., Tulsa, Okla., or 170 Broadway, New York, N. Y. 1000 entries, by author. 90 per cent complete.

Monthly manuscript bibliography of petroleum. E. H. Burroughs, U. S. Bureau of Mines, Washington, D. C. Issued in mimeographed form. Cumulated and published annually as a Bureau bulletin.

Petroleum and natural gas. E. DeGolyer, 65 Broadway, New York, N. Y. 9000 to 10,000 entries, by author and locality. 80 per cent complete.

Petroleum and natural gas: geologic occurrence, statistics and technology. Johnson, Huntley, and Somers, Oil and Gas Bldg., University of Pittsburgh, Pittsburgh, Pa. 7000 entries, by author, subject, and locality. Fairly complete.

Oils from gilsonite. Emmett B. Carmichael, University of Colorado, Boulder, Colo. December 1920–date. Two-thirds complete.

See also **Motor Fuels** (Leslie); **Oil Shale** (McKee).

Petrology:

Chemical analyses of igneous rocks. H. S. Washington, Geophysical Laboratory, Carnegie Institution of Washington, Washington, D. C. 1913–date. Incomplete. Supplement to U. S. Geological Survey, *Professional Paper* 99.

Chemical composition of igneous rocks. Edward B. Mathews, Johns Hopkins University, Baltimore, Md. 9900 entries, by rock names and silica content. Practically complete to date.

Pharmaceutical Chemistry:

Pharmaceutical chemistry and botany. H. V. Arny. Several thousand entries. 1910–date. Abstracts included. For consultation, write College of Pharmacy, Columbia University, New York, N. Y.

Phenanthrene:

The Barrett Co., 40 Rector St., New York, N. Y. 160 entries, by author, subject, and patents. 1900–date. Abstracts included.

Phenols:

Alkali-insoluble phenols. O. M. Brewster, Pullman, Wash. 88 entries. 1881–1920.

Phosphates:

Acid phosphates and superphosphates. A. Marshall, 3043 St. Paul St., Baltimore, Md. Entries by subject. 1880–date

Manufacture and uses of dicalcium phosphate. The Grasselli Chemical Co., Cleveland, Ohio. 21 entries. Abstracts included.

Phosphate deposits. Eliot Blackwelder, 317 Railway Exchange Bldg., Denver, Colo. 415 entries by author and title. Many abstracts included. 80 per cent complete.

Soluble phosphates. Engineering Societies Libraries, New York, N. Y. 52 entries. 1878–1917. Abstracts included.

The Western phosphate field. G. R. Mansfield, U. S. Geological Survey, Washington, D. C. 160 entries, by author. Many abstracts included. 60 per cent complete. To be published later.

Phosphoric Acid:

Patents on phosphoric acid and its salts. William H. Ross, Bureau of Soils, Washington, D. C. 404 entries, by author, title and patent number. Covers whole period of U. S. Patent Office.

Phosphoric acid. Engineering Societies Libraries, New York, N. Y. 81 entries. 1876–1918. Abstracts included.

Phosphorus:

Engineering Societies Libraries, New York, N. Y. 83 entries. 1879–1917. Abstracts included.

Photochemistry:

Action of light on organic compounds, visible spectra with few references to ultra-violet spectra. H. M. McLaughlin, Iowa State College, Ames, Iowa. 332 entries, by author and subject. 1850–1921.

Chemical action of light. Clarence J. West, National Research Council, Washington, D. C. 2000 entries by author. One-half complete.

Light: theory of photochemistry and biological effects. S. C. Brooks, Hygienic Laboratory, 25th and E Sts., N. W., Washington, D. C. Entries by author and subject. Up to 1918 and occasional later entries. Abstracts usually included. 60 to 70 per cent complete.

Photosynthesis and allied subjects. H. A. Spoehr, Carmel, Calif. 450 entries, by author 1797–1922. 95 per cent complete.

Photography:

Physics and chemistry concerned with photography. Research Laboratory, Eastman Kodak Co., Rochester, N. Y. June 1915–date. Printed cards, covering all leading periodicals. Abstracts included.

Phthalic Acid:

Mono-nitro- and monamino-*o*-phthalic acids. M. T. Bogert, Columbia University, New York, N. Y. Over 100 entries, chronological by subject. Up to 1903. Abstracts included. Practically complete.

Piscatorial Chemistry:

Biological, physiological, and technological chemistry of fishes. Harden F. Taylor, Bureau of Fisheries, Washington, D. C. Several hundred entries, by subject. No effort made to include all material found in *Chemical Abstracts*.

Chemistry of fish flesh. Lloyd H. Almy, Bureau of Chemistry, Washington, D. C. 150 entries. Very complete to 1915. Abstracts included.

Pitch Coke:

Pitch coke for carbon electrodes. The Barrett Co., 40 Rector St., New York, N. Y. 82 entries, by author and subject. 1873–date. Abstracts included.

Plant Chemistry:

Effect of nitrates on plants. H. G. MacMillan, Greeley, Colo. 396 entries, by author. 1882–date. Abstracts included in part.

Salt absorption and mineral nutrition of plants. R. B. Harvey, University Farm, St. Paul, Minn. 575 entries, by author and subject. Up to date. Abstracts included in many cases. Nearly all references commonly available.

See also **Soils** (Eaton); **Tobacco** (Gross).

Platinum:

Platinum metals. R. Gilchrist, Bureau of Standards, Washington, D. C. 200 to 250 entries, by title. January 1, 1918–date. Brief abstracts in most cases. All references in *Chemical Abstracts* included.

Poisons:

Economic poisons: substances used for the control of insects, fungi, weeds, and rodents. George P. Gray, State Department of Agriculture, Sacramento, Calif. 20,000 entries, by subject. Covers *Chemical Abstracts* 1911–1920; Experiment Station Record, Vols. 13–24.

Potash:

Potash as by-product from blast furnaces and cement mills. Western Precipitation Co., 1016 W. 9th St., Los Angeles, Calif. 100 entries, by author and title. 1904–date. Abstracts included. Complete.

Potassium Chlorate:

Decomposition of potassium chlorate. F. E. Brown and H. M. McLaughlin, Iowa State College, Ames, Iowa. 175 entries, by author, title, and subject. 1840-date. Abstracts included for about one-half. Must not pass out of owner's possession.

Proteins:

Proteins and accessory factors in nutrition. H. A. Mattill, University of Rochester, Rochester, N. Y. 750 entries, by subject. 1912–date. Abstracts usually included. 90 per cent complete.

Pulp and Paper-Making:

C. E. Libby, New York State College of Forestry, Syracuse, N. Y. 800 entries, by author, title, and subject. 1914-date. Very brief abstracts included. Covers four paper trade journals.

Manufacture, chemical, and physical properties, methods of testing, etc., of pulp and paper. C. J. West, National Research Council, Washington, D. C. 5000 entries, by author, arranged under principal paper-making subjects. One-half complete.

See also **Bagasse** (Little); **Flax** (American Writing Paper Co.).

Pyrazoline:

Pyrazoline derivatives. L. L. Steele, Bureau of Standards, Washington, D. C. 70 entries. Up to and including 1916. Abstracts included. For consultation write either to the Bureau of Standards, Washington, D. C., or Chemical Library, Harvard University, Cambridge, Mass.

Rare Earths:

Rare earths and secondary rare elements. Charles Baskerville. 25,000 entries. Not readily accessible. For consultation, write Library, College of the City of New York, New York, N. Y.

Refractories:

Clay and graphite refractories. H. G. Schurecht, Bureau of Mines, Ceramic Experiment Station, Columbus, Ohio. 75 per cent complete.

Magnesite and dolomite refractories. H. G. Schurecht, Bureau of Mines, Ceramic Experiment Station, Columbus, Ohio. 300 entries, by author, title, and subject. 1873–1921. Abstracts included. Includes six bibliographies and other references obtained from literature, being fairly complete.

Resins:

See **Naval Stores** (Schorger); **Terpenes** (Grotlisch).

Roads:

Surface treatment of roads for laying dust. Arthur D. Little, Inc., Cambridge, Mass. 65 entries, by author.

Rosin:

See **Naval Stores** (Schorger); **Terpenes** (Grotlisch).

Rubber:

Methods of rubber analysis. Frances McGovern, B. F. Goodrich Company, Akron, Ohio. 289 entries, by author and subject. Earliest references to 1920. Abstracts included. Considered complete.

Rubber insulated cable. Arthur D. Little, Inc., Cambridge, Mass. 15 entries, by author.

Salt:

Salt and salines. W. C. Phelan, The Solvay Process Co., Syracuse, N. Y. Entries by author, title, and locality. Complete to date.

Salt, sulfur, and salt domes. E. DeGolyer, 65 Broadway, New York, N. Y. 400 to 500 entries, by author and locality. 80 per cent complete.

Salvarsan:

See **Arsphenamine** (Flick).

Sand:

Glass sands. Charles H. Richardson, Syracuse University, Syracuse, N. Y. 25 additional entries to bibliography published in 1920 in "Glass Sands of Kentucky."

Sericin:

Arthur D. Little, Inc., Cambridge, Mass. 25 entries, by author.

Smoke:

Washing of smelter smoke. F. A. Eustis, 131 State St., Boston, Mass. 330 entries. Up to 1915. For consultation, write to compiler or Library, Harvard University, Cambridge, Mass.

Soap:

Hydrolysis and detergency of soap. L. W. Bosart, Procter and Gamble Co., Ivorydale, Ohio. 80 entries, by title. 1885–1921. Fairly complete.

Sodium Silicate:

William Stericker, Mellon Institute of Industrial Research, Pittsburgh, Pa. 400 entries, by author and subject. 1850–date. Abstracts included.

Soils:

Sulfur content of soils and its relation to plant nutrition. Scott V. Eaton, Department of Botany, University of Chicago, Chicago, Ill. Entries by author and title. 1910–date. Very incomplete.

Sorrel Reaction:

See **Cements** (Schurecht).

Specific Heat:

Specific heat of the elements, also includes heat of fusion and other energy changes. J. E. Mills, Edgewood Arsenal, Edgewood, Md. Entries by author. Up to 1917.

Starch:

Hydrolysis of starch. Arthur D. Little, Inc., Cambridge, Mass. 133 entries, by author.

Steel:

Boiler tube steel. A. E. White, University of Michigan, Ann Arbor, Mich. 17 entries. 1910–1921. Includes most of the pertinent books and articles bearing on the subject.

See also **Alloys** (Estes); **Iron** (Joint Committee on Phosphorus); **Lead Coatings** (Berolzheimer).

Storage Batteries:

Storage batteries; lead plate sulfuric acid type. Paul H. Segnitz, Vesta Battery Corporation, 2100 Indiana Ave., Chicago, Ill. In process of compilation.

Sugar:

Determination of sugars by reduction methods. L. F. Hoyt, Larkin Co., Buffalo, N. Y. 50 entries, by author, title, and subject. 1841–1913.

Development of the sugar industry. Lizin A. Becnel, 1510 Arabella St., New Orleans, La. Numerous entries. Covers a period of 170 years.
See also **Lactose** (Zoller); **Maltose** (Hoyt)

Superphosphate:
See **Phosphates** (Marshall).

Surface Tension:
Jessie Y. Cann, Smith College, Northampton, Mass. Entries by author. Abstracts included.

Tanning:
See **Leather** (Rogers); **Tannins** (Kressmann)

Tannins:
Tannins and the tanning industries. F. W. Kressmann. 3000 entries (316 typewritten pages), by author and subject. Up to 1911. Abstracts included. For consultation, write Forest Products Laboratory, Madison, Wis.

Terpenes:
Terpenes, resins, turpentine, rosin, and their general chemistry. V. E. Grotlisch, Leather and Paper Laboratory, Bureau of Chemistry, Washington, D. C. 500 entries, by title and subject. 1914–date. Abstracts included in some cases. 75 per cent complete.

Textiles:
See **Chemistry** (Mullin); **Waterproofing** (Fenn).

Titanium:
J. F. Haskins, Ohio State University, Columbus, Ohio. 1300 entries, by author. 1789 (time of discovery) to 1921. Abstracts included. Nearly complete.

Tobacco:
Chemistry and manufacture of tobacco. Paul Gross, Trinity College, Durham, N. C. Entries by author and subject. 1850–date (in chemistry); 1700–1919 (in manufacture). Abstracts included in a large portion of the chemistry section. Chemistry section about one-half complete.

Turpentine:
See **Naval Stores** (Schorger); **Terpenes** (Grotlisch).

Vanilla:
Vanilla extract. Arthur D. Little, Inc., Cambridge, Mass. 17 entries, by author.

Vegetable Oils:
See **Fats and Oils** (Thurman).

Viscosity:
Viscosimeters and viscosity (on oils). Charles A. Mann, University of Minnesota, Minneapolis, Minn. 200 entries, by author, title, and subject. Up to 1914. Very complete.
Viscosity: (*a*) General, (*b*) Rubber solutions. G. D. Kratz, The Falls Rubber Co., Cuyahoga Falls, Ohio. Several hundred entries. 1900–1915. Abstracts in almost all cases.
Viscosity (fluidity, plasticity, lubrication). Eugene C. Bingham, Lafayette College, Easton, Pa. 2000 entries, by author. 1500–1921. Complete as possible.

Vitamins:
Walter H. Eddy, Teachers College, Columbia University, New York, N. Y. 800 entries, by author. 1906–1921. Fairly complete. Partially published in his "Vitamin Manual."
J. F. McClendon, Medical School, University of Minnesota, Minneapolis, Minn.

Volumetric Chemical Analysis:
Volumetric chemical analysis, including colorimetric, gasometric, and epimetric methods. Launcelot W. Andrews, Williamstown, Mass. 17,000 to 20,000 entries, by author, title, and subject. 1847–1914. 1914–date, fragmentary. Brief abstracts included.

Water Glass:
See **Sodium Silicate** (Stericker).

Waterproofing:
Waterproofing, mildewproofing, and fireproofing of cotton, linen, and burlap fabrics in the heavier weights. Herbert B. Fenn, Metakloth Co., Lodi, N. J. 1868–1920. Abstracts included in some cases. Far from complete.

Water Softening:
See **Zeolites** (Bartow).

Waters:
Hydrogen-ion concentration of natural waters. F. C. Mortensen, Coe College, Cedar Rapids, Iowa. Abstracts in preparation. Complete.

Wheat:
Wheat milling and baking chemistry and chemical technology. C. H. Bailey, University Farm, St. Paul, Minn. Entries by author and subject. 1900–date. Abstracts included in one-third to one-half of the entries. Nearly complete.

Wood:
The acid hydrolysis of wood. E. C. Sherrard, Forest Products Laboratory, Madison, Wis. 150 entries, by author and subject. 1819–date. Abstracts included. Incomplete. A part is to be published soon in a departmental bulletin.

Wood Preservation:
Wood preservation, with specific reference to protection against marine borers. Clarence J. West. 1000 entries, by author. Two-thirds complete. For consultation, write Committee on Marine Borer Investigation, National Research Council, Washington, D. C.

Wood Tar:
Wood tar and wood-tar oils. The Barrett Co., 40 Rector St., New York, N. Y. 128 entries, by author and subject. 1871–date. Abstracts included.

Zein:
Chemistry of zein. Arthur D. Little, Inc., Cambridge, Mass. 15 entries, by author.

Zeolites:
Use of zeolites in water softening. Edward Bartow and G. C. Baker, State University of Iowa, Iowa City, Iowa. 214 entries, by author. 1907–1921. Abstracts included. Practically complete.

Making Chemistry a White Art

By H. W. Jordan
133 Stolp Ave., Syracuse, N. Y.

Advertising is a principle as fundamental as Kekule's benzol ring. It pays to advertise the American Chemical Society in order to destroy the popular notion that a chemist is a bald-headed, black-capped, back-room hermit, whose characteristic pose is that of looking for a precipitate in an old-fashioned, alembic glass retort filled with malt whiskey.

It was pretty generally noised about during 1917 and 1918 that it was a chemist's war. We admitted it. Now that peace rages, there is little said in the newspapers about its being a chemist's peace. Yet so far as peace is permitted to prevail by prime ministers and Congress, it is the peace of the chemist and engineer. Although the mark and rouble have fallen to ultramicroscopic value, and the price of food, fuel, and housing have grown to be measured almost in units of light years, the chemist produces a ton of pig iron with the same weight of coke and the engineer evaporates the same volume of water with a pound of coal as in 1914.

Since these things are so, why not let the public know it?

In arranging programs for this year, Local Sections of the American Chemical Society can do splendid service for the chemical profession by devoting a part of the lectures to subjects of common interest that will draw big general audiences to assemble with our technical selves. We can climb down from our high scientific niche for a noon hour or an evening to tell folks something of our valuable work in the essential industries of iron and steel, sugar, glass, or soap. We can show people the chemical side of laundry processes, of milk and its products, and of city sanitation. These topics, especially if illustrated, will draw scores where units now attend. At the same time, the lectures can be made as instructing to ourselves as though given before the usual section audience of a couple dozen chemical hardy perennials.

Lots of folks live on top of a thick coal vein, but if it doesn't crop out so that they stumble over it and blacken their hands, they never know the coal is there. Our one hundred million Americans live in a daily world of chemistry, yet only a tiny fraction of them realize it. People say, "Oh, he is a chemist, is he?" in much the same tone as they remark, "How natural he looks," at a funeral.

If we would have our achievements properly valued, we need spread them in the show windows to be admired and appreciated. Rotary Clubs, Chambers of Commerce, Commonweal Clubs, Women's Congresses, and dozens more, comb the country every winter for able speakers on any timely subject. If we expose our chemical orators to this raking, some of them will be joyfully gathered in as star attractions before crowds of business men and women. Thus, our profession of chemistry will get some of its share of deserved publicity. Incidentally, chemists will become more effective citizens.

Electrometric Titration of Sulfurous Acid with Permanganate[1]

By W. S. Hendrixson and L. M. Verbeck

Department of Chemistry, Grinnell College, Grinnell, Iowa

The purpose of this work was to determine whether sulfurous acid in acid solution is completely oxidized to sulfuric acid by an excess of permanganate, as stated in the literature. If so, the excess of permanganate should be easily and accurately determinable electrometrically with potassium iodide, thus giving a simple method for determining sulfur dioxide, sulfurous acid, or sulfites. The results show that with a small or large excess of permanganate only about 90 per cent is oxidized to sulfuric acid, the remainder of the sulfurous acid probably forming dithionic acid.

The practicability of titrating sulfurous acid with permanganate seems so obvious that it is not surprising that it has been attempted by many chemists, although the results have many times been shown to be too low and discordant. For this fact two causes have been assigned, loss of sulfur dioxide and the incomplete oxidation to sulfuric acid by permanganate whether in excess or not. Nearly forty years ago Honig and Zatzek[2] stated that permanganate did not oxidize sulfurous acid completely to sulfuric acid in acid solution, but only in neutral or alkaline solution. In titrating sulfurous acid with permanganate Dymond and Hughes[3] obtained as the average 88.9 per cent of the oxygen used as compared with theory for complete oxidation. By separate experiments on a large scale they definitely proved the formation of dithionic acid when they at the same time ran permanganate and sulfur dioxide into cold water, keeping the sulfur dioxide in excess. They regarded the formation of the dithionic acid as an essential part of the reaction, and due to a stage in the reaction, namely, the reduction of MnO_2 to MnO. Their equation is

$$17H_2SO_3 + 6KMnO_4 = 2K_2S_2O_6 + K_2SO_4 + 6MnSO_4 + 6H_2SO_4 + 11H_2O$$

which would require 88.2 per cent of the oxygen required for complete oxidation to sulfurous acid. They say, however "When a solution of sulfurous acid is poured into an excess of permanganate, only sulfuric acid is formed."

Pinnow[4] carried out several series of titrations of sulfite with permanganate in parallel with titrations by the iodine method. The oxidation to sulfuric acid was never found to be complete. Temperature, concentration, and acidity had little influence. His results varied from 90.9 per cent in acid to 97.2 in alkaline solution. He also assigned the discrepancy to the formation of varying amounts of dithionate.

Possibly encouraged by the statement quoted from Dymond and Hughes, two papers have appeared which propose the determination of sulfurous acid by oxidation with an excess of permanganate. Milbauer[5] added a very dilute solution of the sulfurous acid to ten times the permanganate theoretically necessary to oxidize it to sulfuric acid and determined the excess with oxalic acid. Even though the oxidation were complete, it would be difficult to determine the fact by difference in his method, owing to the large magnification of the unavoidable error in determining such a great excess of permanganate. Sweeney, Outcault, and Withrow[6] added sulfur dioxide or sulfite to an excess of permanganate and determined the excess colorimetrically. They insist on an excess of permanganate at all times. This permanganate was standardized with specially purified sodium sulfite. However, a later communication[7] from the same laboratory showed the impossibility of preparing in weighable condition pure sodium sulfite and called in question all determinations of sulfite based on sodium sulfite as a standard.

Though the preponderance of evidence seemed to be against the complete oxidation of sulfurous acid in acid solution by a moderate excess of permanganate, the question seemed to merit a more rigorous test than had apparently been applied to it, and the electrometric method[8] as applied in the determination of nitrous acid seemed to meet the requirements.

The starting point was a solution of sodium sulfite placed in an atmosphere of hydrogen by use of an apparatus practically the same as that used by Thornton and Chapman.[9] After standing three or four days it was standardized by the iodine method. In all titrations recently boiled water was used and the titrating vessel was kept full of carbon dioxide. Loss of sulfur dioxide was prevented by use of series of bulbs containing iodine and potassium iodide solutions in the standardizations, potassium permanganate in the titrations with permanganate. On account of the rapid change in the concentration of the sulfite solution it was restandardized by the iodine method on the same days that its concentration was determined with permanganate. Though protected in the apparently perfectly working apparatus which maintained an outward pressure of hydrogen equal to about 20-cm. water pressure, the sulfite solution lost daily about 1 per cent of its reducing power. This would require for the average amount of solution stored the access of about 40 cc. of air daily, which seems impossible, and the facts incline one to the view of Shenefield, Vilbrandt, and Withrow[7] that the salt suffers autoxidation.

In carrying out the electrometric determinations with permanganate, a weighed amount of this solution was placed in the titration vessel, an amount of dilute, recently boiled and cooled sulfuric acid was added to make the acid concentration about normal at the end of the experiment, and a rapid stream of purified carbon dioxide was run through the solution for several minutes. The current of gas was slowed down, the mechanical stirrer was started and sufficient sulfite solution was run in to use about half of the permanganate in Series 1, nearly all in Series 2, and to the end-point in Series 3. In Series 1 and 2 the excess of permanganate was destroyed by a slight excess of known potassium iodide and then permanganate was run in until the voltage showed the end-point had been reached. The high degree of uniformity attained by essentially the same method in the determination of nitrous acid[8] was not reached in the titration of sulfurous acid, indicating that the reaction in the latter case is variable, depending upon small differences in conditions that cannot be easily discovered or controlled. Only a few representative determinations are selected for each series. The value of the permanganate was found by sodium oxalate to be 0.05 $N \times 1.033$.

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[1] Received May 15, 1922.

[2] *Monatsh.*, 4 (1883), 738.

[3] *J. Chem. Soc.*, 7 (1897), 314.

[4] *Z. anal. Chem.*, 43 (1904), 91.

[5] *Ibid.*, 48 (1909), 17.

[6] This Journal, 9 (1917), 949.

[7] *Chem. Met. Eng.*, 25 (1921), 953.

[8] Hendrixson, *J. Am. Chem. Soc.*, 43 (1921), 1309.

[9] *Ibid.*, 43 (1921), 91.

SERIES 1—TITRATION OF SULFUROUS ACID WITH A LARGE EXCESS OF PERMANGANATE

Detn.	$KMnO_4$ Reduced Cc.	Excess $KMnO_4$ Cc.	Na_2SO_3 Cc.	H_2SO_3 to 1 Cc.
1	37.61	39.64	21.50	0.00325
2	38.86	41.74	21.95	0.00329
3	51.27	30.88	33.25	0.00326
4	31.28	16.73	20.00	0.00330
			AVERAGE ..	0.003275

The iodine method may not be perfect, but it is the best we have and is doubtless accurate enough for present purposes. Three determinations in parallel by the iodine method gave 0.00352 sulfurous acid in 1 cc. of the sulfite solution, which means that the permanganate gave only 93 per cent of its value.

SERIES 2—TITRATION OF SULFUROUS ACID WITH A SLIGHT EXCESS OF PERMANGANATE

Detn.	$KMnO_4$ Reduced Cc.	Excess $KMnO_4$ Cc.	Na_2SO_3 Cc.	H_2SO_3 to 1 Cc.
1	36.39	4.10	24.95	0.00309
2	37.10	2.84	25.00	0.00314
3	53.20	3.39	36.20	0.00311
			AVERAGE...	0.003113

The iodine method gave at the same date 0.003476, or the permanganate method gave 89.6 per cent of the sulfurous acid present.

Two titrations as shown in Series 3 were made by running the sulfite solution into acidified permanganate to the end-point, with the result that the percentage of oxidation was found not materially different.

SERIES 3—TITRATION OF SULFUROUS ACID WITH PERMANGANATE TO THE END POINT

Detn.	$KMnO_4$ Reduced Cc.	Na_2SO_3 Used Cc.	H_2SO_3 to 1 Cc.
1	44.72	30.50	0.00311
2	63.18	42.60	0.00314
		AVERAGE...	0.003125

The iodine method gave on the same day 0.00340, which is equivalent to 91.9 per cent of the sulfurous acid present.

The conclusion based on our results and the records of the work of others on this subject is that the development of an accurate method for the determination of sulfurous acid with permanganate is impracticable, perhaps impossible.

Some Notes on the Early Indigo Industry in the South[1]

By B. B. Ross

ALABAMA POLYTECHNIC INSTITUTE, AUBURN, ALA.

THE INDIGO industry was one of the oldest, and historically one of the most interesting, of the early chemical industries of the southern states. The precise date of the introduction of indigo culture into this country is somewhat uncertain, but it secured a foothold in several of the southern colonies early in the 18th century.

In Louisiana as early as 1720, planters were furnished indigo seed by the Louisiana Company, and in 1723 the South Carolina Colonial Legislature granted a bounty on indigo to stimulate its production.

By 1746 the industry had reached such a flourishing condition that the bounty was repealed, but the British government by Act of Parliament in 1748 authorized the payment of an export bounty of 6 pence per pound on indigo shipped to the mother country.

According to Dr. D. D. Wallace, professor of history and economics in Wofford College, S. C., the establishment of the culture and production of indigo upon a successful and economic basis was due chiefly to the efforts of a woman, Miss Eliza Lucas, daughter of Governor Lucas of Antigua, and who subsequently became the wife of Col. Charles Pinckney. At her home on Ashepoo plantation near Charleston she carried out numerous experiments connected with the growing of indigo and the preparation for the market, and after encountering many difficulties and discouragements her endeavors met with success and gave a marked impetus to the development of the industry in the colony.

Professor Wallace states that the best results were obtained from growing seed imported from Guatemala, though the indigenous indigo was grown to some extent.

The method of preparation of the crude indigo for the market, as given by the same writer, was as follows:

The entire bush was laid in a stout pine or cypress vat about sixteen feet square and two and one-half feet deep, with the bottom raised about four feet from the ground. This was the *steeper*. A quantity of plants held down by sticks, with weights laid upon them, was immersed in water and left to steep for about twelve hours. The foaming and bubbling due to chemical action being finished, the water was let off through a hole near the bottom into another tank or vat, called the *beater*. In this, the indigo water was agitated violently for several hours by means of paddles—a process usually conducted by hand, but by some planters by means of a paddle wheel somewhat like the stern wheel of a river boat. * * * From time to time lime water was added from a tank or barrel which stood beside the beater.

The master indigo-maker decided from specimens dipped up in a saucer when the flakes had reached the proper degree of precipitation, after which the liquid was left to settle. A fine blue silt collected on the bottom. The liquid above was let off through a succession of holes in the side of the beater and the indigo silt scooped up and reduced by pressure to cakes, which were dried under a shed.

The commercial grades of the product were designated, in the order of quality from highest to lowest, as "fine blue," "ordinary blue," "fine purple," etc., while the most inferior quality was known as "ordinary copper."

As a rule in the southern colonies there were two cuttings of indigo each season, the first in May or June, and the second in September.

The amount of indigo exported from South Carolina in 1748 was 134,118 lbs., which increased to 1,150,662 lbs. in 1775. In Louisiana the exports of the province reached a total value of $100,000 for the year 1769, while in 1775 a single settlement exported 50,000 lbs.

The yield of indigo per acre in the southern colonies ranged from 20 to 100 lbs., the average yield given by one authority being 30 lbs. per acre. The selling price of the product was quoted as ranging from $2^1/_2$ shillings sterling up to $1.20 per lb., and under exceptional conditions as high a figure as $2.25 per lb. was said to have been realized.

The culture and production of indigo in South Carolina, Georgia, and Louisiana, played an important part in the economic and agricultural development of those colonies, and in South Carolina and southeast Georgia the indigo and rice crops were the chief sources of wealth of the large planters near the coast, supplying, as one writer has stated, "the necessary material basis for the rich and cultured low country aristocracy whose influence upon the history of that section has been so powerful."

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[1] From a paper on "Some of the Early Chemical Industries of the South" presented before the Section on History of Chemistry, at the 63rd Meeting of the American Chemical Society, Birmingham, Ala., April 3 to 7, 1922.

As a result of the loss of the English export bounty on indigo, and of the invention of the cotton gin, cotton culture after the Revolution rapidly displaced the growing of indigo in South Carolina and Georgia, while in Louisiana sugar soon became a successful rival of indigo.

Still another factor contributing to the downfall of the industry was the supposedly bad effects of the indigo process upon the health of the operatives. A writer of the period, in discussing this feature of the industry, said, "The whole process was of the most disgusting and disagreeable character, and myriads of flies, generated by it, overspread the whole country. The fetor arising from the putrid weed thrown from the vats was intolerable." Drainage from vats which found its way into streams killed the fish therein and polluted these water courses.

Although the large-scale exportation of indigo ceased before the beginning of the last century, the production of indigo for domestic consumption continued for many years thereafter, and as late as 1845 as much as 35,000 lbs. of indigo were produced in Orangeburg County, South Carolina.

During the Civil War the indigo industry was revived to a certain extent and this important dyestuff was produced in limited quantities to meet the domestic demand.

GRASSELLI MEDAL AWARD

At the meeting of the Society of Chemical Industry at Rumford Hall, New York City, on October 20, 1922, the Grasselli Medal was presented to Mr. Walter H. Fulweiler, chemical engineer of the United Gas Improvement Co., Philadelphia, Pa. This medal is awarded annually by the American Section of the Society of Chemical Industry for the paper presented before that Section which offers the most useful suggestion in applied chemistry.[1] *Mr. Fulweiler is the second recipient of this honor, the first award having been made to Dr. Allen Rogers,*[2] *professor of industrial chemistry at Pratt Institute, Brooklyn, N. Y., for his paper on "Industrial Uses for the Shark and Porpoise."*

Walter H Fulweiler

Presentation

By Harlan S. Miner

The American Section of the Society of Chemical Industry is highly favored in being able to give some tangible recognition to the meritorious papers presented at its meetings. The Grasselli medal and the conditions controlling its award are distinctly American in character. The fact that it is awarded for the paper which, in the opinion of the Medal Committee, offers the most useful suggestions in applied chemistry, makes it peculiarly appropriate in an industrial society. This is only one of many ways in which the donors are advancing the profession of chemistry in the United States.

The Committee of Awards has this year unanimously chosen as the recipient of this honor, Walter Herbert Fulweiler, of Philadelphia, in recognition of the paper which he presented at the March meeting of the Section entitled, "Chemical Problems in the Gas Industry."

The medalist was born in Philadelphia, January 3, 1880, received his preparatory education in the William Penn Charter School, and was graduated from the University of Pennsylvania in 1901, with the degree of B.S. in chemistry.

Having decided to devote his attention to the gas industry, he first accepted a position as chemist at one of the stations of the Philadelphia Gas Works. We next find him as cadet engineer and later as superintendent of manufacture of the Kansas City Gas Company. Returning to Philadelphia in 1907, he entered the Department of Tests of the United Gas Improvement Company, in 1913 becoming chief chemist, and in 1920 chemical engineer for that company.

As might be expected, Mr. Fulweiler's work in connection with the gas industry has been of a very practical nature, and has had a decided economic application, although he has by no means ignored the theoretical or purely scientific side of his subject. With an intimate personal knowledge of the industry both from an American and a European point of view, he constructed one of the first waste heat boilers on a water-gas set. Then he assisted in the design and erection of the first American type of vertical retort at Manchester, N. H.

The utilization of some of the ill-smelling by-products of the gas industry is worthy of note in this connection. Our medalist developed and introduced the successful road-binder produced from water-gas known as "Ugite;" also the first cold patching material made from tar which is now extensively used in road maintenance. In connection with this work, he invented the "cut back" method for manufacturing tar products used in the surface treatment of roads, and also devised an apparatus for determining the binding value of pure bitumens in road construction.

The refining of benzol products as recovered from illuminating gas was thoroughly investigated, particularly with reference to the production of toluene. Like many another loyal chemist connected with our "key" industries, he collaborated with the Ordnance Department during the war, studying particularly the manufacture of toluene. In addition to reporting on several methods for the production of this material so urgently needed at that time, he developed and perfected a process for its manufacture by a heat treatment of California distillates, and assisted in the construction and operation of two plants embodying this process—one at Los Angeles and the other at San Francisco, the former having a production of three million gallons a year at the time of the armistice.

Another subject upon which Mr. Fulweiler worked during the war period was the development of a motor fuel for our Air Service, finally producing one as a by-product from the operation of the toluene process, which under tests at the flying fields enabled the training plane to climb about 5 per cent faster with an economy in fuel consumption of about 8 per cent. This fuel consisted essentially of 60 per cent unsaturated hydrocarbons, 30 per cent benzene, and 10 per cent paraffin hydrocarbons. Refined by a special process, he found by service tests that it was possible to eliminate gumming and corrosion.

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[1] This Journal, 11 (1919), 162.

[2] *Ibid.*, 12 (1920), 1128.

In more recent years our medalist has made an extensive study of the petroleum oils used in the gas industry, with special attention to the development of methods for their identification. These researches, which are still in progress, involve the preparation of a large number of hydrocarbons from different series and then the determination of their physical constants, among which are a number of unusual ones, such as magnetic rotation, electrostatic double refraction, and absorption spectra, particularly in the ultraviolet.

An examination of the many articles from Mr. Fulweiler's pen, and published in various journals, indicates still further the great diversity of his researches and developments. A paper on "Physical Theory of Coal Carbonization" as early as 1908 was awarded the Beale Medal by the American Gas Institute. This was followed by "Theory of Flame and Mantle Illuminosity," "Physical Characteristics of Ferric Oxide," "Purification of Water for Gas-Making Purposes," "A Source of Light, Giving a Continuous Spectrum in the Ultraviolet," "The Development of Modern Road Surfaces," "Destructive Action of Motor Traffic on Road Surfaces," and "Refractory Problems in the Gas Industry."

The subjects of wood preserving and of refractories, both vital to the economic success of a gas plant, have received very careful study, as have also the many intricate problems involved in gas purification. In this field researches have been conducted to determine the nature of the sulfur compounds in illuminating gas, and also the chemical reactions involved in the purification by iron oxide and its subsequent revivification.

These and other papers in addition to the one for which this medal is awarded, demonstrate conclusively that the industry which had its inception over a century and a quarter ago in a relatively crude way, now maintains its important position as a result of systematic scientific research and control. Notwithstanding the volumes that have already been written describing the work of the scientists in this and earlier generations, our medalist has found new fields to investigate and with results that have materially advanced the industry in which he has chosen to labor.

We are glad to find a man who will freely impart of the information obtained through his researches and experience and is willing to publish papers which, as our donors suggest, "offer useful suggestions" to his colleagues.

On behalf of the American Section of the Society of Chemical Industry, I am honored in presenting to you—Mr. Fulweiler—this beautiful medal, not so much as an incentive to spur you on to other and increasing activities, for you do not seem to require such a stimulus, but as a token of appreciation from your many friends in the chemical profession. May you ever see in it an expression of our good will and may it bring you much happiness throughout a long and useful life.

Acceptance

By W. H. Fulweiler

In accepting this beautiful Grasselli medal, I find it difficult properly to express my appreciation of the many complimentary remarks you have made about my work. I am going to refrain from saying the usual things about my unworthiness, as I feel that this would be a reflection of the committee's judgment, and I wish to assure you that I am not unmindful of the honor that has been bestowed on me.

Thirty years ago the gas industry was doomed to early oblivion by the glowing possibilities of electricity. In spite of the tremendous strides of the electrical industry as a competitor, the gas industry to-day employs five times as many men as it did in 1890, its products have ten times their value and the money invested would to-day approximate $4,000,000,000, which is nearly twenty times that invested in the industry in 1890. If the recent predictions of a prominent statistician regarding the early demise of the industry prove to be as correct as the predictions of 1890, we, in the industry, will have little to worry us.

It is true that the gas industry has lost a considerable portion of its lighting business. This has probably been fortunate, rather than unfortunate, as it has undoubtedly been a strong factor in eliminating the candle-power standards which prevented real progress of the industry for so many years.

The future of our industry, as I see it, is to be the delivery of heat energy in the most convenient, efficient, and economical form. A modern carbureted water-gas plant will deliver in the form of salable gas nearly 70 per cent of the heat energy put into the process.

To-day, a great deal of attention is being given to what is called the complete gasification of coal, as by this means we hope to transform even a greater percentage of heat energy in the fuel into gas. The processes that have been evolved to date yield a gas of much lower heating value from that which we are accustomed, being in the neighborhood of 340 B. t. u. per cu. ft., but it may well be that the heating value of the future will approximate this figure.

Technically, the gas industry is in the position of utilizing in everyday practice some of the most complicated chemical and physical reactions with very vague ideas of the mechanism involved, so that there is a large field for research work in determining the "why" of many of our commercial processes. A good start has been made, but there is a tremendous amount of work yet to be done.

I wish to take this opportunity to express my thanks to the Grasselli Chemical Company for its generosity in providing this medal, to the Committee for their consideration in awarding it to me, and to Dr. Miner for the many nice things he has said in presenting the medal to me.

Duplication of Bibliographic Lists and References

One of the first things a research chemist or chemical engineer does in preparation for work on a new problem is to establish the prior art on the subject. This is so essential that hundreds or even thousands of dollars' worth of time may be spent on the search for pertinent literature in various publications. Often distant libraries have to be visited or books borrowed from them. Not infrequently it is subsequently discovered that a complete bibliography on the subject, which would have saved at least half of the time of the searcher, exists. Quite commonly several individuals or industrial concerns simultaneously prepare reference lists or abstracts on the same subject. One notable instance of this sort of wasteful duplication is the compilation of a complete bibliography on the Grignard reaction by Dr. Henry Gilman in Iowa and Dr. C. J. West in Massachusetts working in ignorance of one another's interest.

Bibliographies on scientific and technological subjects are constantly being prepared. Some are published. Some remain in manuscript. It is to the advantage of all investigators to be able to locate such reference lists when they need them. The Research Information Service of the National Research Council, Washington, has established a bibliographic section which aims to serve as a clearing house for information about the sources and availability of both published and unpublished lists of references. The catalog of bibliographies already contains thousands of cards. You are urgently invited to avail yourself of this new aid to research and to further its development by reporting bibliographies of your own which you would be willing to have duplicated or to loan under suitable conditions.

Ernest Solvay—An Appreciation

By William H. Nichols

61 Broadway, New York, N. Y.

THE DISTINGUISHED subject of this sketch, an honorary member of this Society, passed away in his sleep the 26th of May, 1922. It is well for us to pause and take note of some of the salient features of his life, so that those of us who have borne the heat and burden of the day may take renewed courage and pursue our course with determination to the end, and those who are just beginning life may learn what is necessary to attain that success which everyone should strive to achieve.

In an article as brief as this, only certain phases of Mr. Solvay's life and struggles can be considered. It would take a volume to do justice to them all, and to give an adequate idea of the character of the man. He did great things, but what attracts me to him most is not so much what he did, as what he was.

Ernest Solvay was born in the little Brabant town of Rebecq-Rognon, April 16, 1838. His father, a most estimable man, was a refiner of salt on a modest scale. To use Ernest's own words, his "infancy was passed in an atmosphere of chloride of sodium." He had a younger brother, Alfred, of whom he was extremely fond, and who was closely allied to him by bonds of love and mutual understanding during all his early struggles and later successes until called away January 23, 1894. The relations of these brothers were of such an intimate and touching nature that taken alone they will repay a careful study in these days when family affection and loyalty are not too frequently in evidence. After Alfred's death until his own final hour, Ernest's regard for him became a real religion. He would never consent to receive praise unless his brother's name was coupled with his own. Let us, therefore, in speaking of Ernest, remember how much Alfred should be considered as part of him—a loyal co-laborer.

Ernest passed several years at a boarding school in Malonne. He was planning a university course, but a grave malady obliged him to give this up—a bitter disappointment, as we can imagine. So he returned to his native village and kept his father's books. He naturally had considerable leisure, which he employed in reading elementary books on chemistry and physics. He was not long in putting some of his new-found knowledge into practice by making experiments in chemical combinations and reactions.

His uncle, Mr. Semet, was director of a small gas works at Schaarbeek. In 1860, Ernest was called to be his assistant, and here a new life began on a wider plane. He had always been familiar with salt, and now he added a knowledge of the preparation and properties of ammonia. In a year he had discovered and patented in Belgium the reactions now known as the Ammonia-Soda, or Solvay process, utterly unaware of work, without result, by several predecessors. Soon after began that memorable struggle to apply his discovery, which seemed so many times to be at the brink of failure, but which ultimately emerged so magnificent a success, owing to his dauntless courage and faith in himself. We must remember that chemical engineering was not very far advanced in 1861, and this young man was neither a chemist nor an engineer as we understand the terms. That he became both later was much to his credit, and furnishes another instance of the efficiency of hard knocks.

In 1861, a small experimental plant was installed at Schaarbeek. On December 28 of that year, Ernest writes:

> Our apparatus is now in order and I believe nothing prevents beginning our experiments. If all goes as I have foreseen, as all I have been able to try out up till now—apparatus, different combinations—all will go well. As far as I am concerned, however, I do not put too much faith in them and expect to have to make changes, for it would indeed be almost unheard of if everything were to succeed in an undertaking of this importance, and, moreover, entirely new. I have never been in doubt, and at present less than ever, of the success of the apparatus itself, and of the great advantage which there would be in operating on an industrial scale. What I cannot answer for, as indeed no one in my position could, is that I will see all my combinations succeed at the first attempt. I made a summary beforehand of all the difficulties which might arise, and already a certain number of these have been cleared up. No trouble has arisen in so far as my own conceptions are concerned.

Six days later, on January 4, Mr. Solvay wrote:

> I believe that I can now tell you something serious, something really certain. If I have ever had the slightest doubt as to the value of my process in so far as its industrial application is concerned, it would now be completely cleared. On Monday, we put all the apparatus in operation, working on 100 kilos of material; everything went perfectly smoothly. All I had foreseen in so far as the ease, the regularity and the practical side of the process were concerned, was far surpassed.

Difficulties arose, and on June 4, 1862, after a shutdown of three weeks given up to repairs and new preparations, Mr. Alfred Solvay wrote:

> We began to operate by trying out each apparatus, one at a time; all went well until yesterday. During the night we found that the pump was no longer drawing water. The well was dry, and we had to stop. This is a new delay, but as is always the case it does not come from the process itself! We really have had bad luck with our equipment! And we had had to work like horses day and night!

That same year, the two brothers and their foreman were nearly asphyxiated by an escape of gas, and were only saved by the lucky return of a workman who carried them into the open air. Experiments went on, however. When the trials were considered sufficiently advanced, negotiations were opened up in view of interesting two industrial companies in the enterprise, but without success.

Negotiations were then begun with Mr. Pirmez, and after six months Solvay & Co., with headquarters at Couillet, was founded on December 26, 1863. This was the first step. The second was no less difficult. It lasted until the end of October 1865, when the works were shut down after the most important unit had given way.

The year 1864 was passed in construction work and negotiations of all sorts. Before the end of the year it became necessary to issue a certain amount of new stock to increase the company's capital which was insufficient.

On December 15, 1864, everything was ready to begin work again, and Mr. Solvay wrote:

> I spent yesterday and last night at Couillet trying out the new apparatus with water. All the units show leakages but nothing serious***. I am quite satisfied with the general result. When the repairs are completed we will have another trial, and I hope that by New Year we will be able to run the proper raw material through. Our well has not been giving enough water. We will have to run a pipe line to the Sambre which will take about eight days, unless there is an exceptional frost.

Of course there was a frost, but that was only the beginning of new difficulties, and on January 4, 1865, Alfred Solvay wrote:

> Ernest arrived and we worked all day Sunday, we did not realize that it was the first of January. A bad leak had just broken out in the distilling apparatus. Everything had been going so smoothly! There had already been a leak, but we had been able to get around this difficulty by not using this particular part of the apparatus. Isn't it rough luck when we had taken such care and gone to such trouble?

Bad luck, however, continued. On June 26, 1865, it was decided to put the works in run again. Mr. Alfred Solvay writes at that date:

> We may still have setbacks, but with the changes we have made we have great hope. Let us hope that this time all will go well, and that Ernest will finally be rewarded for so much energy, courage, perseverance, and sacrifice of every sort. Poor boy, he has already suffered a great deal!

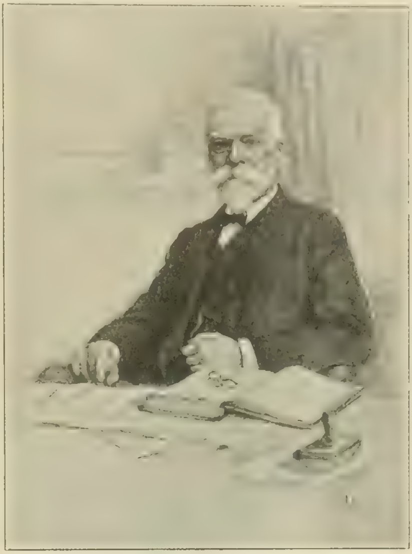
In the meantime, the production reached 600 to 800 kilos a day.

Mr. Ernest Solvay writes at this time.

> All our efforts have always been aimed at keeping going, if only a few days at a time, on a basis of 2 to 3,000 kilos in order to form a definite opinion of our affair. We always see the promised land in the distance without being able to reach it.

He ended his letter of August 3, 1865, as follows:

> The process will win out. Of this I am absolutely certain, but much perseverance must still be applied. Our task is not yet finished. All would go more quickly if we were able to go straight ahead when we see what there is to be done, but we are in a situation which calls for reflection.



E. Solvay

The situation which he mentions so delicately was financial.

On June 26, 1865, in the midst of almost insurmountable difficulties, Mr. Ernest Solvay had made an admirable report to Mr. Pirmez, in which he definitely stated his faith in the future of the process, giving as reasons, the enormous production of soda ash in the world, the lowering in the future of the cost of production to the extent necessary to take the place of sulfate of soda in the glass industry, the manufacture of soda crystals and the utilization of residues—in short, a complete program of what was to be realized later. In October a crack appeared in one of the units, but the apparatus was kept going by lowering the pressure and by admitting more gas. Bad luck, however, followed the brothers. A few weeks later the main unit blew up, carrying away, it would seem, their last hopes. They were completely broken down. Ernest felt that he was losing his hold on himself in the midst of so much misfortune; something had to be done. It was in such terms that a member of the family stated the case by letter, for it was in the midst of their family at Rebecq that the two Solvay brothers withdrew to comfort themselves, with their mother who was confident in the efforts of her sons, as all mothers should be, and with their sister. At this time, Mr. Ernest Solvay was married and his wife gave him that wonderful moral support which was to enlighten all his life. The works were shut down under pretext of repairs. The winding up of the affairs of the company was imminent, but this eventuality was avoided, for at this moment the Solvay parents gave their son a mark of confidence and abnegation which was to save them. They made a last sacrifice and put 40,000 more francs into the business. The two young men took up the fight anew. In a touching way we are given an opportunity of appreciating the conflict which was going on in the mind of the inventor. Mr. Solvay writes:

> If I am at times discouraged it is because I feel that I am in vain weighed down under all this burden, because I feel that despite my will power I am losing confidence in my strength. I am afraid to go on for fear of wearing myself out still further.

But this letter closes with a burst of enthusiasm:

> I believe that I am capable of making a last effort, and of regaining sufficient energy to forget all, or at least a great deal, and to consider the work that I am about to do as a trial.

Finally on February 18, 1866, Mr. Ernest Solvay ends his letter in these terms:

> We reached our 1,000 kilos mark at the end of last week. The product is superb. If we can go on a fortnight in this way, it will be as clear as day that our manufacturing problem is solved, and we must complete it and put ourselves at ease in so far as material is concerned. Let us hope that this time we will have attained success, and been able to prove it. There are so many reasons for desiring this.

Eight days later success was no longer in doubt, and Mr. Solvay writes:

> After being so often within an inch, within a hairs-breadth of failure, can I finally succeed in regaining from others and from myself, that moral strength which the entire world seems to refuse me. After all that has happened, this would indeed be a splendid triumph! Let us not speak of it, we are too accustomed to setbacks and deceptions.

On July 1, 1866, at the time when the Austro-German war had just been declared all continued to go well, but then he writes:

> Had it not been for the war we could consider ourselves saved. This is indeed about the last straw.

Eight days later, however, a letter brings out the fact that for three days in succession production had reached 1,300 kilos:

> We are working to reach 1,500 or 2,000 kilos. Then only will I believe that we are saved.

A month later, the daily production of 1,500 kilos became a regular thing; all was saved.

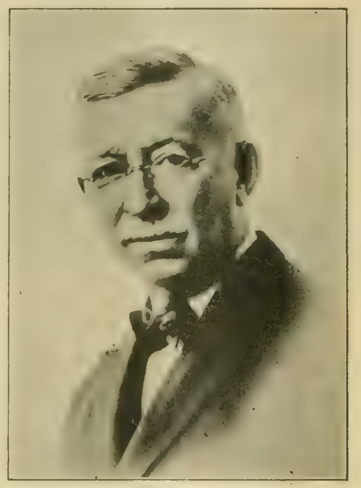
Space prevents further quotations. All the world knows what happened after this; plants to utilize the process were constructed in many countries, including our own, and the price of soda the world over came down by leaps and bounds. Neither can we pause to consider the immense influence this had in the whole field of chemical operations. Where others failed, a complete success had been scored. And yet, with all the concrete results, the story shows conclusively that the man was much greater than his works. He succeeded in the face of what seemed insurmountable difficulties, because of his character.

His character. There is no mystery about that. It shone out in every walk of life, and in every problem that presented itself—simple, courageous, studious, affectionate, honest, and thoroughly human. We find him excelling as an Alpinist, climbing nearly every peak. We find him giving deep thought and study to the amelioration of his fellowmen. We find him, with these dreams and hopes shattered by the World War conditions in 1914 taking the lead in the movement so wonderfully seconded in our own country, to feed and clothe the unhappy people of Belgium. We find him endowing educational institutions of various sorts. We find him always doing good. But we never find him seeking the spotlight. He sought the approval of his own conscience and I am sure he received it. He did not under-rate the value of the encomiums of his fellowmen, but these were a consequence and not an objective.

He lived a happy life, except during those terrible years of the Occupation. As old age came creeping on, he gave up one responsibility after another to those he had so well prepared to bear them. Nothing was forgotten. His life was complete. The words of his father he had made his own: "Work is a debt that all true citizens owe to society."

AMERICAN CONTEMPORARIES

Edgar Fahs Smith



Edgar Fahs Smith

OPENING the door of a quiet study, softly lighted from high windows, walls lined with books and rare prints of eminent chemists of the ages—glimpsing here an ancient lock wrested from the door of Priestley's laboratory in Birmingham as it was destroyed by the mob, there a delicate balance brought by the aged exile to America—one senses contact with a *personality* before one sees, seated at the desk, the quiet figure of the man, Edgar Fahs Smith—teacher, administrator, author, chemist. Human, and of a generous and lovable nature, with a handclasp firm, warm, and sincere, his quiet smile puts one immediately at ease. Sympathy and strength seem to radiate from his person. A most friendly man, he makes friends and keeps them in all parts of the world. Not in a weak optimism, but in virile strength and sound judgment he thinks kindly of human nature.

A son of the soil of Pennsylvania, of pioneer American descent, educationally the product of an old-fashioned college curriculum, broadly trained in the humanities, specializing later in chemistry in a foreign university, a pupil of Wöhler—Dr. Smith's keen and correct appreciation of persons and policies, his power of concentration, of rapid and effective accomplishment of details demanding his attention, the never-flagging energies of his efforts, are qualities that have made him a marked man, and caused his University, his State, and the Nation to press him into services quite foreign to those of his chosen guild—chemistry.

A teacher of chemistry for 44 years, 21 of which were combined with administrative service, first as Vice Provost and then Provost of the University of Pennsylvania, Dr. Smith's career may be summed up as one which for length and richness has seldom, if ever, been equaled in the history of American collegiate education. An enthusiastic, inspiring teacher, an able and efficient administrator, he fairly won the title of the "best beloved college president of his generation."

Dr. Smith is a firm believer in the creed that it is better to wear out than to rust out, and his intense industry and happy disposition furnish a living example of the joy of work. Gifted with rare ability as an investigator, his contributions in chemistry have made his name familiar to students of science throughout the world. More than 200 scientific papers have been published by him, as well as numerous books on chemistry. His monumental work on "Electro-Analysis" has reached six editions and has been translated into French, German, Italian, and Russian. Tungsten, molybdenum, columbium, tantalum, the separation of rare earths, and the constitution of complex inorganic acids, have particularly engaged his attention. His work in the field of atomic weights is characterized by marked originality.

In his valuable contributions to the field of historical chemistry, Dr. Smith has accomplished that rare thing—the imparting of literary charm to a scientific subject. Opening a door more than a century old, he has let us peep at the babyhood of American chemistry. In his biographies of Robert Hare, James Cutbush, James Woodhouse, in "Priestley in America," and in "Chemistry in America" he has put flesh on the skeletons of pioneers in the science, making them living, breathing personalities, depicting their struggles and achievements in a manner inspiring to patriotic Americans of the present generation.

Other pages list the honors and rewards which have come to this man of many-sided interests. Thrice elected to the office of President of the AMERICAN CHEMICAL SOCIETY, his administrations have been characterized by untiring work for the protection of American chemical industries that America may be free from foreign domination, by aiming to build up American chemical literature, by urging a broader education for chemists as a proper foundation upon which to build for research, and by emphasizing the study of what American chemistry has done that American work, already large, may be appreciated.

Service, yes, in the highest sense of the word—service to mankind—so runs the record of Edgar Fahs Smith.

W. T. TAGGART

SCIENTIFIC SOCIETIES

Standard Methods for the Sampling and Analysis of Commercial Soaps and Soap Products[1]

The *Committee on Methods of Analysis and Specifications of Commercial Soaps and Soap Products* of the *Division of Industrial Chemists and Chemical Engineers* of the AMERICAN CHEMICAL SOCIETY has given careful consideration to criticisms of its previous report[2] and has also coöperated with the Soap Committee of the American Specialty Manufacturers' Association and with the Technical Committee on Soaps of the U. S. Government, with the result that the following report was unanimously adopted April 3, 1922.

ARCHIBALD CAMPBELL, *Chairman*, The Globe Soap Co., Cincinnati, Ohio.
C. P. LONG, The Globe Soap Co., Cincinnati, Ohio.
J. R. POWELL, Armour Soap Wks., Chicago, Ill.
PERCY H. WALKER, Bureau of Standards, Washington, D. C.
R. E. DIVINE, Armour Soap Wks., Chicago, Ill.

APPLICABILITY OF THE METHODS

It is admitted that the methods of sampling may not in all cases yield samples that are truly representative of the whole lot, but any method that would do so would be so cumbersome and expensive as to defeat its own purpose.[3] The methods given do not favor either buyer or seller, and are believed to be as accurate as the economic considerations warrant, and if mutually agreed upon should be satisfactory to all interested parties.

The methods of test differ somewhat in form, and in some cases in substance, from those given in the previous report, because the committee has attempted to cover methods that would be of importance in commercial transactions rather than methods that would be mainly of theoretical interest and only applicable in special cases. As presented, the methods of sampling and testing can be directly applied to commercial transactions, and it may be of interest to state that the methods prescribed in the specifications for various soap products recommended as U. S. Government Standards by the Federal Specifications Board are essentially the same as these.

A—SAMPLING

The seller shall have the option of being represented at the time of sampling and when he so requests shall be furnished with a duplicate sample.

I. CAKE SOAPS, FLAKE AND POWDERED SOAP PRODUCTS, WHEN PACKED IN CANS OR CARTONS—One cake (can or carton) shall be taken at random from not less than 1 per cent of the vendors' shipping containers, provided such containers contain not less than 50 lbs. In the case of smaller containers, a cake (can or carton) shall be taken at random from each lot of containers totaling not more than 5000 lbs. The total sample shall in all cases consist of not less than three cakes (cans or cartons) taken at random from separate containers. With very large lots where the sample drawn as above will amount to more than 20 lbs., the percentage of packages sampled shall be reduced so that the amount drawn shall not exceed 20 lbs.

Wrap the individual cakes (cans or cartons) tightly in paraffined paper at once and seal by rubbing the edges with a heated iron. The inspector shall accurately weigh each wrapped cake (can or carton), record its weight and the date of weighing on the wrapper, place the wrapped cakes (cans or cartons) in an airtight container which should be nearly filled, and seal, mark, and send to the laboratory for test. Samples should be kept cool until tested.

II. FLAKE AND POWDERED SOAP PRODUCTS WHEN IN BULK—A grab sample of not less than $^1/_2$ lb. shall be taken at random from not less than 1 per cent of the vendors' shipping containers, provided such containers contain not less than 100 lbs. In case of smaller containers, a grab sample of not less than $^1/_2$ lb. shall be taken at random from each lot of containers totaling not more than 10,000 lbs. The total samples shall in all cases consist of not less than three grab portions taken at random from separate containers. With very large lots where the sample drawn as above will amount to more than 20 lbs., the percentage of packages sampled shall be reduced so that the amount drawn shall not exceed 20 lbs. The inspector shall rapidly mix the sample, place in an airtight container, which shall be filled, and seal, mark, accurately weigh, record its weight and date of weighing on the package, and send to the laboratory for test. Samples should be kept cool until tested.

III. LIQUID SOAP—A sample of not less than $^1/_2$ pt. shall be taken at random from not less than 1 per cent of the vendors' shipping containers, provided such containers contain not less than 10 gal. each. In case of smaller containers, a sample of not less than $^1/_2$ pt. shall be taken at random from each lot of containers totaling not more than 1000 gal. The total sample shall in all cases consist of not less than three portions of $^1/_2$ pt. each taken at random from separate containers. Before drawing the sample from the container selected, the contents of the container shall be thoroughly agitated. The inspector shall thoroughly mix the samples drawn, place in clean, dry cans or bottles, which shall be completely filled and securely stoppered with clean corks or caps; seal, mark, and send to the laboratory for test.

IV. PASTE SOAP PRODUCTS—(1) *When packed in cans or cartons of 5 lbs. or less.* One can or carton shall be taken at random from not less than 1 per cent of the vendors' shipping containers, provided such containers contain not less than 50 lbs. In case of smaller containers, a can or carton shall be taken at random from each lot of containers totaling not more than 5000 lbs. The total sample shall in all cases consist of not less than 3 cans or cartons taken at random from separate containers. With very large lots where the sample drawn as above will amount to more than 20 lbs., the percentage of packages sampled shall be reduced so that the amount drawn shall not exceed 20 lbs. Wrap, seal, mark, and send to laboratory for test.

(2) *When packed in bulk.* Take a trial sample at random of not less than $^1/_2$ lb. from not less than 1 per cent of the vendors' shipping containers, provided such containers contain not less than 50 lbs. In case of smaller containers a trial sample shall be taken at random from each lot of containers totaling not more than 5000 lbs. The total sample shall in all cases consist of not less than 3 half-pound portions taken at random from separate containers. With very large lots where the sample drawn as above will amount to more than 10 lbs., the percentage of packages sampled shall be reduced so that the amount drawn shall not exceed 10 lbs. The inspector shall promptly place the combined sample in a clean, dry, air- and watertight container, which shall be filled, and seal, mark, and send to the laboratory for test.

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[1] Approved by the Supervisory Committee on Standard Methods of Analysis, American Chemical Society, July 29, 1922.

[2] THIS JOURNAL, **11** (1919), 785.

[3] Sampling and testing small shipments is more or less impracticable, as the expense is in most cases greater than any differences that might be involved.

B—PREPARATION OF SAMPLES

I. CAKE SOAP—In case of samples that can be easily disintegrated and mixed, run the entire sample through a suitable chopper. When the sample is large, each cake may be quartered and one-quarter of each cake run through the chopper. With samples that cannot be handled as above, select a cake of average weight, quarter it by cutting at right angles in the center and shave equally from all freshly cut surfaces sufficient soap for analysis. Mix and weigh out all portions for analysis promptly. Preserve the remainder in an airtight container in a cool place.

II. POWDERED AND CHIP SOAPS—Rapidly disintegrate and mix the sample; if desired, quarter down to about 1 lb. and weigh out all portions for analysis at once. Unused portions of the sample for analysis shall be preserved in an airtight container in a cool place.

III. LIQUID SOAP—No preparation of the sample, other than thorough mixing, is necessary unless it is received during very cold weather, when it should be allowed to stand at least 1 hr. after it has warmed up to room temperature (20° to 30° C.) before it is noted whether it forms a satisfactory lather.

IV. PASTE SOAP PRODUCTS—Mix thoroughly by kneading and quarter down to about 1 lb. Weigh out all portions for analysis promptly and preserve remainder in an airtight container in a cool place.

C—METHODS OF ANALYSIS

When a determination shows nonconformity with the specifications, a duplicate shall be run.

I. MATTER VOLATILE AT 105° C.—Weigh 5 g. of the sample in a porcelain or glass dish about 6 to 7 cm. in diameter and 4 cm. deep, dry to constant weight in an inert atmosphere at a temperature not exceeding 105° C.

II. TOTAL MATTER INSOLUBLE IN ALCOHOL. FREE ALKALI OR FREE ACID—(1) *Matter insoluble in alcohol.* Digest hot a 10-g. sample with 200 cc. of freshly boiled ethyl alcohol neutral to phenolphthalein (94 per cent or higher). Filter through a counterpoised filter paper neutral to phenolphthalein, or a weighed Gooch crucible with suction, protecting the solution during the operation from carbon dioxide and other acid fumes. Wash the residue on the paper, or in the crucible, with hot neutral alcohol until free from soap. Dry the filter paper, or crucible, and residue at 100° to 105° C. for 3 hrs., cool, and weigh the total matter insoluble in alcohol.[4]

(2) *Free alkali or free acid.* Titrate the filtrate from the above, using phenolphthalein as indicator, with standard acid or alkali solution, and calculate the alkalinity to sodium hydroxide (or potassium hydroxide), or acidity to oleic acid.

(3) *Matter insoluble in water.* Proceed as in the determination of matter insoluble in alcohol. After filtering and thoroughly washing the residue, extract it with water at 60° C., and wash the filter thoroughly. (When the matter insoluble in water is all inorganic, boiling water may be used for the extraction and washing.) Dry the filter and residue at 100° to 105° C. for 3 hrs., cool, and weigh matter insoluble in water. The nature of this matter may be determined by further examination.

(4) *Total alkalinity of matter insoluble in alcohol.* (*Alkaline salts.*) Titrate the filtrate from the determination of matter insoluble in water with standard acid, using methyl orange as indicator. Calculate the alkalinity to sodium oxide (Na_2O), and, if desired, to any other basis agreed upon by the parties interested.

III. COMBINED ALKALI. TOTAL ANHYDROUS SOAP—Dissolve 5 to 10 g. of the sample, depending upon the anhydrous soap content, in 100 cc. of water in a 250-cc. Erlenmeyer flask. When solution is complete, add dilute sulfuric acid in slight excess, insert a small funnel in the neck of the flask, and heat the flask at a temperature not exceeding 60° C. until the fatty acids separate as a clear layer. Transfer to a separatory funnel, draw off the acid layer into a second separatory funnel and shake the acid aqueous liquid with two 20-cc. portions of ethyl ether. Dissolve the fatty acids in the ether used for washing the aqueous liquid and shake with 10-cc. portions of water until they are no longer acid to methyl orange. Unite the water portions used for washing and shake with 20 cc. of ether. Wash this ether until the wash water is neutral to methyl orange. Save the acid water for chloride determination. Unite the ether solutions (if necessary, filter, washing the paper with ether) in a suitable weighed vessel, add 100 cc. of neutral alcohol free from carbon dioxide, add phenolphthalein and titrate to exact neutrality with standard sodium hydroxide solution. Evaporate off the alcohol, dry to constant weight as in the determination of matter volatile at 105° C. and calculate the percentage of soda soap. This soap naturally includes any mineral oil and neutral fat, which, if determined separately, must be deducted from the result to obtain the true soap. Calculate the combined sodium oxide (Na_2O) and deduct from the weight of soda soap to give the anhydrides. If the original soap was potash soap, proper calculation must be made to reduce to potassium oxide (K_2O), or the titration made directly with standard potassium hydroxide solution. In case the soap shows an excess of free acid, proper corrections must be made in calculating the combined alkali in the original soap.[5] (See determination of rosin.) With soaps containing a large amount of soluble silicates and soap products containing a high percentage of finely divided material insoluble in water, the foregoing procedure cannot be applied as given. In such cases the filtrate obtained in the determination of total matter insoluble in alcohol can be used after neutralizing any free acid or alkali. Evaporate off the alcohol on a steam bath, take up in water and proceed as above.

With soap products containing a high percentage of matter insoluble in alcohol where approximate results will suffice, such as may be the case with cleansers, soap powders, scouring compounds, pastes, etc., and where agreed upon by the parties interested, the alcoholic solution, obtained after filtering off and washing the matter insoluble in alcohol, may be evaporated directly in a weighed vessel, dried at 105° C. to constant weight, and the result reported as soap.

IV. CHLORIDE—Neutralize with chlorine-free alkali the acid water obtained in paragraph C–III. Titrate with standard silver nitrate solution, using potassium chromate as indicator, and calculate the result to sodium chloride or potassium chloride as the character of the soap indicates.

In case the total anhydrous soap is not to be determined it will be more convenient to use the following method:[6] Dissolve 5 g. of the sample in 300 cc. of water, boiling if necessary to effect solution. Add an excess of neutral, chlorine-free magnesium nitrate solution (about 25 cc. of a 20 per cent $Mg(NO_3)_2.6H_2O$ solution). Without cooling or filtering, titrate with standard silver nitrate solution, using potassium chromate as indicator.

V. UNSAPONIFIED AND UNSAPONIFIABLE MATTER—Weigh 5 g. of the soap into a beaker and dissolve in about 100 cc. of 50 per cent alcohol on the steam bath. If the sample has been found to contain free fatty acid, add just enough aqueous alkali to neutralize this. Evaporate off the bulk of the alcohol, take up with about 200 cc. of hot water and transfer to a separatory funnel of about 500-cc. capacity, designated as No. 1. When cool, rinse out the beaker with about 50 cc. of ether and add it to the soap solution. Shake thoroughly for one minute. By the addition of small amounts of alcohol (5-cc. portions and the total not to exceed 25 cc.), a clear and rapid separation of the aqueous and ether layers is effected. After adding each alcohol portion, the separatory funnel is not shaken but merely given a whirling movement. Draw off the aqueous portion into another separatory funnel, designated as No. 2. Wash the ether solution with 10-cc. portions of water until this water is no longer alkaline to phenolphthalein. Add all these washings to Funnel No. 2 and extract this solution with 20-cc. portions of ether until the ether is absolutely colorless (3 or 4 extractions should be sufficient). Combine these ether extracts in a third separatory funnel (No. 3) and wash with 10-cc. portions of water until the water is no longer alkaline to phenolphthalein. Now add the ether in Funnel 3 to that in Funnel 1, a small amount of ether being used to rinse out Funnel 3. Wash the ether solution with 20 cc. of 10 per cent hydrochloric acid solution and then successively with 20-cc. portions of water until the water is no longer acid to methyl orange. Filter the ether solution through a dry filter paper into a weighed beaker or flask. Evaporate or distil off the ether on the steam bath, dry as under the determination of matter volatile at 105° C. and weigh the residue, then heat with alcohol and, when cool, neutralize with standard alkali, using phenolphthalein. Deduct any appreciable amount of fatty acid found by this titration from the weight of the residue. This residue consists of the unsaponifiable matter and any neutral fat that may have been present in the soap. In case it is desired to separate these, thoroughly saponify the residue with alcoholic alkali and repeat the foregoing procedure. The residue obtained is unsaponifiable matter only.

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[4] The matter insoluble in alcohol will contain most of the alkaline salts, such as carbonates, borates, silicates, phosphates and sulfates, as well as starch, and may be used for the approximate determination of these constituents. These salts are not entirely insoluble in alcohol, so for accurate determinations separate portions of the soap should be used.

For determination of carbonates see C–XI; phosphates, C–XII; sulfates, C–XIII; silicates, C–XX; borax, C–IX; starch, C–XIV(4).

[5] A blank test should be made on the sodium or potassium hydroxide solution for neutral salts and the proper corrections made if necessary.

[6] H. C. Bennett, THIS JOURNAL, 13 (1921), 813.

VI. ROSIN—*Wolff's method.*[7] Dissolve 5 g. of the sample in 100 to 200 cc. of hot water, add a slight excess of dilute sulfuric acid, heat until the fatty acids collect in a clear layer, cool to room temperature, extract with a small portion of ether, draw off the water layer and wash the ether solution with water until free from mineral acid. Transfer to a 200-cc. Erlenmeyer flask, evaporate off the ether and dry 1 hr. at 105° C., cool and dissolve in 20 cc. of absolute alcohol. Then add 10 cc. of a solution of one volume of concentrated sulfuric acid (sp. gr. 1.84) and 4 volumes of absolute alcohol, and boil on the steam bath for 4 min. under a reflux condenser. Remove from steam bath, add to the liquid about 5 times its volume of 7 to 10 per cent sodium chloride solution, and extract with ether. Shake out the aqueous portion 2 or 3 times with ether. Unite the ether solutions and wash with sodium chloride solution until the washings are neutral to methyl orange. Add 30 cc. neutral alcohol, and titrate the rosin acids with standard sodium hydroxide solution, using phenolphthalein as indicator. Calculate to rosin or rosin soap, as desired (1 cc. normal alkali = 0.346 g. rosin or 0.377 g. rosin soda soap). If the true fatty acid soap is desired, subtract the rosin soap from the total anhydrous soap obtained under C–III.

VII. TITER TEST—(1) *Preparation of total fatty matter (fatty and rosin acids and unsaponified matter).* Dissolve about 50 g. of soap in 500 cc. of hot water, add 100 cc. of 30 per cent sulfuric acid, heat until the fatty matter collects in a clear layer, siphon off the acid layer and wash the fatty matter free from sulfuric acid with hot water. Decant the fatty matter into a dry beaker, filter, using a hot-water funnel, or placing both funnel and receiving beaker in a water-jacketed oven, and dry for 20 min. at the temperature of boiling water.

When other determinations are to be made on the total fatty matter, and volatile and readily oxidizable fatty acids are present, the following method should be used: Dissolve about 50 g. of the soap in 300 cc. of hot water, transfer to a separatory funnel, add 150 cc. of approximately 2 N sulfuric acid, cool somewhat, add 120 cc. of ether, shake, draw off the acid layer, and wash the ether layer free from acid with a strong salt (NaCl) solution. Then draw off the aqueous layer as completely as possible, transfer the ether layer to a flask (it is not necessary to transfer quantitatively), add 20 to 30 g. of anhydrous sodium sulfate, stopper the flask, shake, and let stand at a temperature below 25° C. until the ethereal liquid becomes perfectly clear, showing that all water has been taken up by the sodium sulfate. Filter through a dry paper into another Erlenmeyer flask, and completely evaporate off the ether by passing through the flask a current of dry air and heating the flask to a temperature not above 50° C.

(2) *Determination.*[8] (*a*) *Thermometer.* The thermometer shall be a standard titer thermometer graduated at zero and in tenth degrees from 10° to 65° C., and certified by the U. S. Bureau of Standards.

(*b*) *Procedure.* Transfer the fatty acids prepared as under VII(1), when cooled somewhat, to a titer tube 25 mm. by 100 mm. placed in a 16-oz. salt-mouth bottle of clear glass 70 mm. by 150 mm., fitted with a cork that is perforated so as to hold the tube rigidly when in position. Suspend the titer thermometer so that it can be used as a stirrer and stir the fatty acids slowly (about 100 r. p. m.) until the mercury remains stationary for 30 sec. Allow the thermometer to hang quietly with the bulb in the center of the tube and report the highest point to which the mercury rises as the titer of the fatty acids. The titer should be made in a room at about 20° C. for all fats having a titer above 30° C. and at 10° C. below the titer for all other fats.

VIII. ACID NUMBER OF FATTY ACIDS—(1) *Preparation of fatty acids.* Follow procedure given under C–VII.

(2) *Determination.* In a 250-cc. Erlenmeyer flask dissolve 2 g. of the fatty acids, accurately weighed, in 20 to 30 cc. of neutral 95 per cent ethyl alcohol. Titrate with standard alkali, using phenolphthalein as indicator. Calculate the acid number (mg. of KOH per g. of fatty acids).

IX. BORAX DETERMINATION[9]—Weigh 10 g. of the soap (or 5 g. if more than 5 per cent of borax is present) into a platinum dish and add 2.15 g. of fusion mixture (consisting of 200 g. sodium carbonate, 15 g. silica in fine powder). To this mixture add 15 cc. of alcohol, mix with the aid of a glass rod and, after washing the rod with a little alcohol, evaporate the mass to dryness on the water bath. Ignite until the combustible material is destroyed, cover the dish with a piece of platinum foil and fuse. Completely disintegrate the fusion by boiling with water and transfer the solution to a 250-cc. round-bottom flask. Acidify with 20 cc. of dilute hydrochloric acid (1:1), heat nearly to boiling, and add a moderate excess of dry precipitated calcium carbonate. Connect with a reflux condenser and boil vigorously for 10 min. Filter out the precipitate through a folded filter, washing several times with hot water, but keeping the total volume of liquid below 100 cc.

Return the filtrate to the flask, add a pinch of calcium carbonate and again boil under a reflux condenser. Remove the flame and connect the top of the condenser with a water pump. Apply the suction until the boiling has nearly ceased. Cool to ordinary temperature, add 50 cc. of neutral glycerol and titrate the solution with 0.1 N sodium hydroxide, free from carbonate, using phenolphthalein as indicator. After the end-point is reached add 10 cc. more of glycerol and again titrate. Repeat this process until the addition of glycerol causes no further action on the end-point. The number of cubic centimeters required multiplied by 0.00955 will give the equivalent of borax ($Na_2B_4O_7.10H_2O$) present in the solution.

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[7] *Chem.-Ztg.*, **38** (1917), 369, 382, 430; *C. A.*, **8** (1914), 2495.

[8] [illegible] 1920, [illegible] Fat Analysis Committee Method, THIS JOURNAL, **11** (1919), 1163.

[9] Poetschke, *Ibid.*, **5** (1913), 645.

X. DETERMINATION OF SILICA PRESENT AS ALKALINE SILICATES—When the material contains no mineral matter that is insoluble in water, ignite a sample of the soap containing not to exceed 0.2 g. of silica in a platinum dish at a low temperature. When charred, extract the soluble salts with water, return the paper and charred residue to the dish and complete the ignition. Unite the residue in the dish and the water extract, carefully acidify with hydrochloric acid, finally adding the equivalent of from 5 to 10 cc. strong hydrochloric acid in excess. The dish or casserole containing the solution should be covered with a watch glass while adding acid so as to avoid loss by spray.

When the material contains mineral matter insoluble in water, or a determination of highest accuracy is not necessary, take a portion of the solution after titrating the matter insoluble in alcohol C–II(4) containing not more than 0.2 g. silica and add 5 to 10 cc. strong hydrochloric acid.

Evaporate the acidified solution (washing off and removing the cover glass if used) to dryness on steam bath or hot plate at a temperature not exceeding 200° C. Cool, moisten with concentrated hydrochloric acid, let stand 5 to 10 min., breaking up all lumps with a stirring rod. Add about 25 cc. of hot water. Heat a few minutes and filter through a small ashless paper. Wash thoroughly with hot water.

Evaporate the filtrate to dryness and repeat the above treatment, filtering on a second paper. Carefully ignite the two papers and contents in a weighed platinum crucible, first at a low temperature until the paper is consumed, but finally heating to constant weight over the blast lamp; cool in a desiccator before weighing. If extreme accuracy is desired, moisten the contents of the crucible with water, add 10 cc. hydrofluoric acid and 4 drops of strong sulfuric acid, evaporate to dryness over a low flame, ignite at the temperature of the blast lamp for about 2 min., cool in a desiccator and weigh. The difference between this weight and the previous weight is the weight of the silica (SiO_2).[10]

To calculate sodium silicate ($Na_2Si_4O_9$) multiply weight of SiO_2 by 1.26.

XI. DETERMINATION OF CARBON DIOXIDE (CARBONATES)—For most determinations the dry matter insoluble in alcohol as obtained in C–II(1) will be suitable for this determination. In some cases it might be desired to run the test directly on an original sample of the soap. This should always be done when the highest accuracy is required. Any reliable absorption method for determining carbon dioxide may be used.[11]

The following is a method which has proved satisfactory:

A 250-cc. Erlenmeyer flask is placed on a gauze over a burner. The flask is equipped with a 2-hole rubber stopper, through one opening of which is a 10-in. reflux condenser and through the other a thistle tube equipped at the outer end with a 3-way stopcock. The lower end of the thistle tube is drawn to a small point, which is placed very close to the bottom of the flask. To the straightaway end of the stopcock is attached a small funnel for the introduction of acid to the flask. The other opening of the stopcock is attached to receive air from a purifying train consisting of a wash bottle containing concentrated sulfuric acid and a second at the outer end of the train containing a 50 per cent solution of potassium hydroxide. The top of the reflux condenser is attached first to a drying wash bottle containing concentrated sulfuric acid, and then to a weighed absorbing train consisting of a suitable potash bulb charged with 50 per cent potassium hydroxide, and a second containing concentrated sulfuric acid. This train is attached to a protective U-tube containing calcium chloride. The U-tube is attached to an aspirator.

Procedure. Set up the apparatus, leaving out the weighed train, and aspirate with a slow stream of the dry carbon-dioxide-free air until the apparatus is freed from carbon dioxide. Insert the train and continue the aspiration for $^1/_2$ hr. Check the weight of the train to determine if the air is passing through too fast, or if the system is free from carbon dioxide. The system must be free from leaks. Weigh out 1 or 2 g. of the sample into the Erlenmeyer flask, cover with 20 cc. freshly boiled distilled water, close the apparatus with the train in place. Add 20 cc. dilute hydrochloric acid (1 : 1) through the funnel very slowly, with no heat being applied to the flask. The rate of adding acid should be carefully controlled so that the gas does not pass through the train too rapidly. As soon as the acid is added, start aspiration gently. When the absorption begins to stop the gas flow, start heating gently and continue until the contents of the flask have boiled 15 to 20 min. Stop heating and continue aspirating until the flask has cooled down. Remove the train and weigh. Calculate increase of weight as carbon dioxide. Carbon dioxide multiplied by 2.41 equals sodium carbonate.

XII. DETERMINATION OF PHOSPHATES[12]—If a qualitative test has shown the presence of phosphates and their determination is desired, the matter insoluble in alcohol C–II(1) or the ash from the incineration of an original sample can be used. An original sample should always be used when the highest accuracy is desired.

(1) *Reagents.* (*a*) *Molybdate solution.* Dissolve 100 g. of molybdic acid in dilute ammonium hydroxide [144 cc. of ammonium hydroxide (sp. gr. 0.90) and 271 cc. of water]; pour this solution slowly and with constant stirring into dilute nitric acid [489 cc. of nitric acid (sp. gr. 1.42) and 1148 cc. of water]. Keep the mixture in a warm place for several days or until a portion heated to 40° C. deposits no yellow precipitate of ammonium phosphomolybdate. Decant the solution from any sediment and preserve in glass-stoppered vessels.

(*b*) *Ammonium nitrate solution.* Dissolve 200 g. of commercial ammonium nitrate, phosphate-free, in water, and dilute to 2 liters

(*c*) *Magnesia mixture.* Dissolve 110 g. of crystallized magnesium chloride ($MgCl_2 . 6H_2O$) in water, add 280 g. of ammonium chloride, 261 cc. of ammonium hydroxide (sp. gr. 0.90), and dilute to 2 liters.

(*d*) *Dilute ammonium hydroxide for washing.* Dilute 100 cc. of ammonium hydroxide (sp. gr. 0.90) to 1 liter.

(2) *Determination.* Weigh out a 2-g. sample of the alcohol-insoluble or ash, and proceed as in C–X for removal of silica, saving the filtrate. Make up to 250 cc., concentrating if necessary. Take an aliquot corresponding to 0.50 g. or 1 g., neutralize with ammonium hydroxide, and clear with a few drops of nitric acid. Add about 15 g. of dry ammonium nitrate or a solution containing that amount. To the hot solution add 70 cc. of the molybdate solution for every decigram of phosphoric acid (P_2O_5) present. Digest at about 65° C. for an hour, and determine if the phosphoric acid has been completely precipitated by the addition of more molybdate solution to the clear supernatant liquid. Filter and wash with cold water or, preferably, ammonium nitrate solution. Dissolve the precipitate on the filter with ammonium hydroxide and hot water, and wash into a beaker to a bulk of not more than 100 cc. Nearly neutralize with hydrochloric acid, cool, and from a buret add slowly (about 1 drop per sec.), stirring vigorously, 15 cc. of magnesia mixture for each decigram of phosphoric acid (P_2O_5) present. After 15 min. add 12 cc. of ammonium hydroxide (sp. gr. 0.90). Let stand till the supernatant liquid is clear (2 hrs. is usually enough), filter, wash with the dilute ammonium hydroxide until the washings are nearly free from chlorides, ignite to whiteness or to a grayish white, weigh, and calculate to phosphoric acid (P_2O_5), or alkaline phosphate known to be present.

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[10] "The Analysis of Silicate and Carbonate Rocks," by W. F. Hillebrand, *U. S. Geol. Survey, Bull.* **700**, 102.

[11] "Methods of Analysis of Assoc. Official Agr. Chem.," **1920**, 277, *Bur. Chem., Bull.* **107**, 169.

[12] "Methods of Analysis of Assoc. Official Agr. Chem.," **1920**, 1.

XIII. DETERMINATION OF SULFATES—For most determinations the matter insoluble in alcohol obtained under C–II may suffice. If a determination of the highest accuracy is desired, ignite a 10-g. sample of the soap and use the ash from the ignition. Digest with 100 cc. of water, cover with a watch glass, and neutralize carefully with hydrochloric acid. When neutralized, add 5 cc. excess of hydrochloric acid, filter, and wash the residue thoroughly.[13] Make up the filtrate to 250 cc. in a beaker, and boil. To the boiling solution add 15 to 20 cc. 10 per cent barium chloride solution slowly drop by drop from a pipet. Continue boiling until the precipitate is well formed, or digest on a steam bath over night. Set aside over night or for a few hours, filter through a prepared Gooch crucible, ignite gently, and weigh as barium sulfate. Calculate to sodium sulfate, or the alkaline sulfate known to be present.

XIV. DETERMINATION OF GLYCEROL, SUGAR, AND STARCH—(1) *Determination of glycerol in the absence of sugar.*

SOLUTIONS REQUIRED
Potassium Dichromate, 74.552 g. per liter
Sodium Thiosulfate, 0.1 *N*
Potassium Iodide, 10 per cent

Dissolve an accurately weighed sample of the soap[14] equivalent to not more than 3.0 g. of glycerol in 200 cc. of hot water in a 600-cc. beaker. Decompose with 25 cc. sulfuric acid (1:4). If alcohol is present, volatilize it by boiling for 20 to 30 min. Cool, remove, and rinse the cake of fatty acids, transfer the acid water and rinsings to a 500-cc. graduated flask, add about 0.25 g. silver sulfate to precipitate traces of chlorides and soluble fatty acids. Make up to volume and mix contents thoroughly.

Transfer a filtered, accurately measured 50-cc. aliquot of the above to a 400-cc. beaker, to this add 75 cc. accurately measured potassium dichromate solution, followed by 25 cc. of sulfuric acid (sp. gr. 1.84). Cover with a watch glass, and oxidize by heating in a steam bath for 3 hrs. Conduct a blank in like manner but using 100 cc. of water, 25 cc. of sulfuric acid (sp. gr. 1.84), and 25 cc. accurately measured potassium dichromate.

Cool and make up the solution to 1000 cc. in graduated flasks. The excess of potassium dichromate is determined by taking 50 cc. aliquot of the above, adding 50 cc. of water, 20 cc. of 10 per cent potassium iodide solution, and titrating the liberated iodine with 0.1 *N* thiosulfate, using starch solution as indicator.

Calculate the percentage of glycerol (1 cc. of the potassium dichromate solution equals 0.0100 g. of glycerol).

(2) *Determination of sugar.*[15] Dissolve 10 g. of the soap in 200 cc. of hot water in a 600-cc. beaker. Decompose with 25 cc. of sulfuric acid (1 : 4), boil gently for 20 min. to invert the cane sugar completely. Cool, remove, and rinse the cake of fatty acids. Extract the acid liquid with 25 cc. of ether. Transfer the acid liquid to a 500-cc. graduated flask, make up to volume and mix thoroughly. Determine invert sugar in 50 cc. of this solution by the Munson-Walker Method.[16] To calculate sugar (sucrose) multiply the amount of invert sugar found by 0.95.

(3) *Determination of glycerol in the presence of sugars.*[17] Proceed as above under (1), taking a sample so that the sum of the glycerol and sugar is not more than 3.0 g.[18] The solution must be boiled in all cases at least 20 min. to insure complete inversion of cane sugar. Determine the amount of potassium dichromate solution required to oxidize both the sugar and glycerol. Determine also the sugar by the method given in (2).

Calculate the percentage of glycerol after deducting the amount of potassium dichromate required by the sugar.

1 cc. potassium dichromate equals 0.0100 g. glycerol.
1 cc. potassium dichromate equals 0.01142 g. invert sugar.

(4) *Determination of starch.*[19] Separate the matter insoluble in water as under C–II(3), using a sample of soap that will give not more than 3 g. of starch. Transfer the insoluble matter, without drying, to a beaker and heat for 2$^{1}/_{2}$ hrs. with 200 cc. of water and 20 cc. of hydrochloric acid (sp. gr. 1.125) in a flask provided with a reflux condenser. Cool, and nearly neutralize with sodium hydroxide. Complete the volume to 250 cc., filter, and determine the reducing sugars by the gravimetric method as given under method for the determination of sugar.

Calculate the amount of dextrose (*d*-glucose) equivalent to the cuprous oxide obtained. This multiplied by 0.90 equals the amount of starch.

XV. VOLATILE HYDROCARBON—Weigh not less than 250 g. of the sample into a flask of about 5-liter capacity, which is so placed on a gauze that it can be heated. Add 2 to 3 liters of distilled water. Place a 2-holed rubber stopper in the flask, through one hole of which is inserted a copper or brass tube extending into the flask and terminating in a small circular ring of the tubing, bent so that the ring is in a horizontal position. Numerous small holes are drilled in the upper side of this ring and the end of the tube is sealed. This ring should be near the bottom of the flask.

Through the other hole of the stopper is inserted a glass tube provided with a trap of suitable form, the upper end of which is bent so as to be connected with a plain Liebig condenser. The end of the condenser tube is bent so as to extend into a buret graduated to 0.1 cc.

Introduce steam (free from oil) into the flask through the brass tube and collect the distillate in the buret. When the buret becomes full, draw off the water by opening the stopcock. The foam which forms in the flask may be controlled by momentarily shutting off the steam and by regulating heat applied to the flask.[20]

Read from time to time the amount of hydrocarbon distillate which collects on the top of the water in the buret, and when there is no further increase in this distillate the operation is finished. Allow the buret to stand over night, tightly stoppered, and then, after reading the amount of distillate, draw off the water as carefully as possible. Determine the specific gravity of the distillate, and calculate the weight and percentage in the original sample.

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[13] Evaporation to dryness is unnecessary unless gelatinous silica should have separated, and should never be performed on a bath heated by gas. See Hillebrand, *U. S. Geol. Survey, Bull.* **700**, 232.

[14] If starch is present, it will be necessary to remove the matter insoluble in water as described under this determination [C–II (1) and (3)]. Combine the alcohol and water solutions, evaporate off the alcohol, and proceed.

[15] If starch is present, see footnotes 13 and 18, and determination of starch XIV(4).

[16] *J. Am. Chem. Soc.*, **28** (1906), 663; *Bur. Chem., Bull.* **107**; "Methods of Analysis of Assoc. Official Agr. Chem.," **1920**, 78.

[17] Hoyt and Pemberton, THIS JOURNAL, **14** (1922), 54; Correction, **14** (1922), 340.

[18] See footnote 13, if starch is present.

[19] "Methods of Analysis of Assoc. Official Agr. Chem.," **1920**, 95; *Bur. Chem., Bull.* **107**, 53.

[20] Some find it an advantage to add 200 to 300 g. calcium chloride to the flask containing the soap solution, to prevent foaming.

Editors of Journal of Physical Chemistry

The following have been elected editors of the *Journal of Physical Chemistry* under the coöperative agreement published on page 91 of Proceedings of the AMERICAN CHEMICAL SOCIETY, for October 1922.

CHEMICAL SOCIETY OF LONDON: Prof. T. M. Lowry, Prof. J. W. McBain, and Prof. J. C. Philip.

FARADAY SOCIETY: Prof. F. G. Donnan.

AMERICAN CHEMICAL SOCIETY: Dr. A. L. Day, Prof. G. A. Hulett, Dr. Irving Langmuir, and Prof. W. L. Miller.

The editor-in-chief will be elected by this board.

Report of the Viscosity Committee of the Cellulose Division[1]

To the Cellulose Division of the American Chemical Society:

Your special committee on viscosity determination, appointed at the Rochester meeting, begs to present the following report. Your committee has carefully considered the possibility of standardizing a method for determining the viscosity of cellulose ester solutions in order to obtain a uniform standard for specifying this property, particularly in the buying, selling, and using of such solutions.

Early in June 1921, a questionnaire was sent out to the larger manufacturers and users of cellulose ester solutions in the United States, telling them what the committee planned to do and asking if their coöperation could be counted on. Although two replied that they were not interested, sixteen assured the committee of their coöperation. That there was an obvious need for the work that the committee planned to do, was indicated by the fact that most of the replies used such expressions as "We recognize the value of such a standard and we will be greatly interested in the work of your committee;" "We are heartily in favor of the movement and will gladly coöperate with you;" "Think it desirable that one standard method be adopted;" "We are thoroughly in favor of standardizing a method for use in determining the viscosity of nitrocellulose solutions."

These replies also showed that of the sixteen concerns sending favorable replies nine used the falling ball method and a number of these used it exclusively. Two concerns used the MacMichael viscometer, but no other method was used by more than one concern. In other words, the falling ball method was in most common use, and therefore the logical thing to do seemed to be to standardize the conditions of this method.

On sending out a second questionnaire inquiring about eleven variable conditions in this method, only one was the same in any two laboratories and that one was uniform in all of the nine from whom replies were received. In considering these various conditions, it was recognized that in the strictly scientific sense it is not possible to measure "viscosity" by the falling ball method, since cellulose ester solutions are not true viscous liquids but really plastic materials in which the consistency depends on the so-called yield value or force required to start the mass flowing and also on the mobility or ease of flowing after it has once started. The committee does not feel, however, that this distinction is of importance in a method for general practical use, provided only that it is realized that the property being measured is not true viscosity. The main object is to standardize the method so that different users will use identical conditions, and therefore of necessity obtain close agreement in measuring the *apparent* viscosity of a given solution.

It is hoped that the suggested method will be adopted for regular factory use by most, if not all, of the manufacturers and users of cellulose ester solutions. This is the more necessary because in using different rates of shear the *apparent* viscosity may conceivably vary within very wide limits. If it is not possible for a given manufacturer to adopt this method, it is suggested that the manufacturer or user determine the ratio between his particular apparatus and the standard apparatus for solutions of widely different *apparent* viscosity and then write his specifications in accordance with the standard apparatus.

The proposed method consists, in brief, of allowing a 0.635 cm. ($^1/_4$ in.) steel ball to fall through the solution of which the viscosity is to be measured, the solution being contained in a cylindrical glass tube. The time in seconds which is required for the ball to pass between two marks 25.4 cm. (10 in.) apart is the viscosity in seconds. The apparatus should conform to the following specifications:

	Centimeters	Inches
Height of tube..................At least	33	13
Inside diameter........................	3.5	$1^3/_8$
Distance between marks...............	25.4	10
Distance from top of tube to upper mark...........................	5	2
Distance from lower mark to bottom of solution................At least	2.5	1
Height of liquid above upper mark......	2.5	1
Diameter of ball......................	0.635	$^1/_4$
Temperature of solution to be maintained by a water jacket within.....	±0.5° C.	
Material of ball.......................	Steel	

Delivery of ball—The ball is to be released at the top of a small glass tube 4.5 cm. ($1^3/_4$ in.) long, the lower end of which shall dip into the solution 0.6 cm. ($^1/_4$ in). The small glass tube through which the ball is to be delivered shall be of such an inside diameter that the ball will just slip through without binding. This delivery tube shall be maintained in a vertical position by passing it through the center of a stopper which fits the top of the wider tube containing the solution.

Measurement of time of fall—The time shall preferably be measured with a stop watch, tested and found accurate to 0.2 sec.

The committee recognizes and wishes to call attention to the fact that there are advantages in reporting viscosity measurements in terms of centipoise units, since the results obtained at one time will then always be comparable with those obtained later, even if changes have in the meantime been made in the details of the viscometer. In the case of the falling ball method, the formula for this conversion is $V = K(S-S')T$, where

V = the viscosity in centipoises
S = the density of the ball
S' = the density of the liquid
T = the time of the fall in seconds
K = a constant for the apparatus

The constant K for every apparatus is best obtained by standardizing against a liquid of known viscosity, and for this purpose castor oil is very satisfactory. The Bureau of Standards will determine the viscosity of a sample of castor oil at any one temperature for \$2.00. The density of castor oil can be obtained from the tables in the literature within the limits of accuracy of the method. The time of fall for a large ball in castor oil is so short that it cannot be accurately measured, and for this reason it is probably best to use $^1/_8$-in. steel balls rather than the larger ones which are to be regularly used. The ratio between $^1/_8$-in. steel balls and $^1/_4$-in. steel balls is approximately 3 : 1. It should be noted again that the value thus calculated does not, strictly speaking, represent viscosity, since cellulose ester solutions are not true viscous liquids; but the results will be of value in a practical way.

It is recommended (1) that, if the method as specified meets with the approval of the members of the Division, it be submitted for further approval to the Supervisory Committee on Standard Methods of Analysis of the AMERICAN CHEMICAL SOCIETY, (2) that, subject to this approval, a vote be passed designating this method as "The Tentative Standard Method of the Cellulose Division, AMERICAN CHEMICAL SOCIETY, for Determining the Viscosity of Cellulose Ester Solutions by Means of a Falling Ball," and (3) that this report be published in *The Journal of Industrial and Engineering Chemistry*.

It is further recommended that arrangements be made to have the method tried out in a number of laboratories to determine how closely different manipulators will check one another on the same example, a further report to be made at the next meeting on this phase of the matter. If the method proves reliable in practice, the word "Tentative" can then be dropped from the title and the method finally adopted as "Standard."

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[1] The report of the Viscosity Committee of the Cellulose Division was presented at the Pittsburgh meeting, and is being published in accordance with a vote of the Division. In its present form it is only tentative and it is hoped that all those interested will forward their suggestions and criticisms to the chairman of the committee, G. J. Esselen, Jr., 248 Boylston St., Boston 17, Mass. Some suggestions have already reached the committee and these will be taken into consideration in preparing the final report.

It is further to be hoped that laboratories having occasion to determine the viscosity of cellulose ester solutions will coöperate with the committee to the extent of giving the proposed method a thorough trial, in order that any weaknesses may be shown up and corrected.

The committee wishes to acknowledge the valuable suggestions given by Mr. Winslow H. Herschel, of the Bureau of Standards, and by the various manufacturing firms who have been kind enough to give the committee information regarding the methods in use by them for determining viscosity.

GUSTAVUS J. ESSELEN, JR., *Chairman*
C. P. BEISTLE
EUGENE C. BINGHAM
HAMILTON BRADSHAW
W. J. WAITE

American Institute of Chemical Engineers

The 15th Annual Meeting of the American Institute of Chemical Engineers will be held at Richmond, Va., on December 6 to 9, 1922.

Reports for the year of the various committees and officers will be rendered and new officers elected for the coming year.

The program of papers will include the following, most of which are included in a symposium on "Materials of Construction:"

Wood. J. V. N. DORR.
Oil Substitution Products. W. B. PRATT.
Chemical Stoneware. P. C. KINGSBURY.
Use of Propane for Refrigeration. H. D EDWARDS.
Effect of Rate of Flow on Absorption of Gases. WALLACE B. VAN ARSDEL.
Resistance of Packing to Fluid Flow. F. C. BLAKE.
Absorption and Scrubbing Tower Design. R. T. HASLAM.
Methods of Attacking Evaporation Problems. H. K. MOORE.
Asbestos Protected Metal. J. H. YOUNG.
Volume Changes in Portland Cement Structures. A. H. WHITE.

Opportunity will be offered for visiting the following plants in Richmond and vicinity: The Richmond Chemical Works, a subsidiary of the Virginia-Carolina Chemical Co., acid, phosphate, and fertilizer manufacturers; plants of R. J. Reynolds Tobacco Co., and Larus & Brother Co., manufacturers of chewing tobacco, cigarettes, and smoking tobacco; Richmond Cedar Works, the largest wood works in the world; Atlantic Varnish Works; Richmond Forgings Corporation; American Glass Works; Richmond Guano Co.; Albemarle Paper Manufacturing Co.; C. F. Sauer Co.; Southern Manufacturing Co.

The Hotel Jefferson will be convention headquarters.

The membership of the Local Committee is as follows:

W. T. DABNEY, Business Manager of the Chamber of Commerce, *Chairman*.
JOHN G. ARMISTEAD, Lefebvre-Armistead Co., Merchandise Brokers.
GEORGE H. NASH, Virginia-Carolina Chemical Co.
JULIUS B. WEEMS, Chief of the Department of Chemistry, State Department of Agriculture.
J. B. ROBB, Robb & Arnold, Analytical Chemists.
HENRY FROEHLING, Froehling & Robertson, Analytical Chemists.
SAMUEL H. SHEIB, Froehling & Robertson.

Calendar of Meetings

American Association of Textile Chemists and Colorists—1st Annual Meeting, New York City, December 2, 1922.

American Institute of Chemical Engineers—Richmond, Va., December 6 to 9, 1922.

American Ceramic Society—Annual Meeting, Pittsburgh, Pa., February 12 to 17, 1923.

American Chemical Society—65th Meeting, New Haven, Conn., April 2 to 7, 1923.

American Electrochemical Society—43rd Semiannual Meeting, New York City, May 3 to 5, 1923.

Papers for Program of Industrial Division

In order that more time can be given to the presentation and discussion of papers delivered before the Division of Industrial and Engineering Chemistry of the AMERICAN CHEMICAL SOCIETY, it has been decided to ask all who plan to give papers before this Division to submit completed manuscripts not later than March 1 to the Secretary of the Division. The manuscripts will then be sent to reviewers just as articles now submitted to any of the journals of the SOCIETY are treated. Upon favorable recommendation of the reviewers and the officers of the Division, the papers will be included in the final program of the Division.

It has been keenly felt for some time that something must be done to raise the standard of some of the papers that have been given before the Division. In some cases old material has been redescribed under a new heading, which often was misleading. No doubt the new method will reduce the number of papers to be presented at any one meeting, but it is felt that a few genuinely good papers followed by a sufficient time for discussion will be what most chemists desire. At Pittsburgh there were so many papers on the program that a time limit of seven minutes was allotted with three minutes for discussion. This time proved to be so short that a speaker could not present the paper in the best manner, and the period for discussion was so short that there was practically no attempt on the part of members to discuss the subject.

Since the spring meeting occurs at New Haven, April 2 to 7, inclusive, it is necessary for members of the SOCIETY who are planning to present papers before this Division to send their papers on or before March 1 to the Secretary of the Division.

ERLE M. BILLINGS, *Secretary*

KODAK PARK
ROCHESTER, N. Y.

American Electrochemical Society

Spring Meeting Announcement

The 43rd General Meeting of the Society will be held in New York City, with headquarters at the Commodore Hotel. The meeting will take place May 3, 4, and 5, 1923.

A committee, consisting of Irving Fellner, *Chairman*, H. B. Coho, and Chas. F. Roth, has already started making arrangements for the accommodation and comfort of members and their guests. The large local membership, the accessibility of New York from all points, and the interesting symposia in course of preparation are but a few of the reasons why this meeting should be one that will break all previous attendance records.

Dr. F. M. Becket is making extensive arrangements for a symposium on the "Rarer Metals" which is bound to give rise to interesting and enthusiastic discussions. This symposium will include papers on "The Production and Application of the Rarer Metals," such as vanadium, tungsten, cobalt, molybdenum, zirconium, cerium, uranium, tantalum, calcium, magnesium, and others.

Another symposium, on "Electrode Potentials," in charge of Dr. Wm. G. Horsch, will take place at this meeting and will include studies on reversible electromotive force, overvoltage, ion activities, electro-titration, and pH determinations.

Members submitting manuscripts for this meeting of the Society are kindly requested to forward two copies of their manuscripts to the Secretary by January 15, 1923, and not later than February 1, 1923, as this is the closing date for accepting papers.

The 1922 Meeting of the Association of Official Agricultural Chemists

After an interval of several years, the Association of Official Agricultural Chemists returned to the Raleigh Hotel, Washington, D. C., for its 38th Annual Meeting, November 15 to 17. There were more than 350 members and visitors present. The usual reports of referees, associate referees, and committees were presented.

Honorable Henry C. Wallace, Secretary of Agriculture, welcomed the chemists to Washington in behalf of the Department of Agriculture. He stressed the importance of coördinating the work of the various branches of the Government, using as illustrations the different activities of his own department in grain and cotton, and pointed out the great opportunities that such coördination will unfold for the chemist.

On Thursday, the regular sessions were interrupted sufficiently long to listen to some special addresses. First came a concise but live talk by the president, F. P. Veitch, on "Opportunities and Responsibilities of the Association of Official Agricultural Chemists." He urged the members to advise the secretary of any proposed outside activity which would come in any way within the field of the association so that steps might be taken to coördinate the various efforts and avoid duplication of work. He stressed the importance of promoting uniformity in methods, the interchange of ideas, of at least one representative from each member organization attending the annual meetings of the society, and recommended that the association revert to its former practice of printing the full report of the annual meetings, including all discussions. In addition to work on methods and their application, the president urged the members to take a larger directing part in all scientific service relating to agriculture and to give all the information they have to give when service, private or public, involving chemistry is performed.

Then came an address by Dr. Harvey W. Wiley, honorary president—the man who has the rare distinction of never having missed a meeting of the association. This is a happy circumstance for those attending these conventions, since his address is always regarded as the bright spot of the meeting. Always timely in his remarks, it being Cancer Week, he discussed the cancer question. He regarded it as peculiarly appropriate to address chemists on this subject since one of the remedial agents for cancer has been provided by the action of chemists. He spoke in scathing terms of the misleading advertisements for cancer that are being broadcasted, considering them one of the greatest enemies of cancer cures. Commenting upon the remarkable change that has taken place in our ideas of the nature of matter, our present-day belief that all matter is alike—that all the electrons in the nucleus are the same wherever they exist—in his inimitable manner he compared the history of the atom to the history of humanity, likening the protons to men and the electrons to women. In conclusion he said that the unknown will always offer endless fields and opportunities for investigation, and that there is no end to the good which this association can accomplish—it is boundless in its activities and in its field of endeavor. He urged chemists to cultivate the true scientific spirit, never to be satisfied, but to keep on with perfect humility even in the attainment of great progress.

Senator E. F. Ladd of North Dakota, many years actively engaged in association work, first as referee, then as a member or chairman of various important committees, and at one time president, next addressed the convention. He seemed happy to be in a gathering of chemists and declared that he felt more at home with them than he has ever felt among politicians. He believes that there is no greater field than that of chemistry and that the future holds even greater possibilities for the chemist. National laws, in regard to paint, varnish, and textile, will probably be enacted at an early session of Congress. Such laws will throw added responsibility upon our regulatory officials and will open new fields of endeavor both for the regulatory and research worker. These laws will be for the best interest of the people and, in the end, for the manufacturers themselves. Need for reform in expert testimony was emphasized, and chemists were urged not to allow the lawyer to determine what they shall give as evidence. Very often the chemist allows the attorney to shape the answer so that it suits the attorney's ideas and thus the chemist only presents a half-proof, which frequently leads to wrong decisions. He urged chemists to insist that they formulate their own questions and their own answers in court cases, and called attention to the importance of the

[illegible]

service which the association could render in this respect. The Senator paid special tribute to Dr. Wiley as the guiding spirit of the association and said that he had come before the association to meet the chemists with whom he had been associated in the past, and to show his good will and respect for the great calling of chemistry.

So much interest was manifested in the Drug Section that the program, instead of occupying half a day as scheduled, continued for more than one and one-half days. In all, eighteen reports and papers were presented. Methods were adopted as official for the examination of arsphenamine and neoarsphenamine. This is the first time the association has had official methods for these substances. Very notable action was taken when the association went on record as recommending that the methods for the assay of physostigma and its preparations and fluid extract of hyoscyamus be submitted to the chairman of the revision committee of the United States Pharmacopeia, and that these methods remain tentative until such time as they appear in the Pharmacopeia. Mr. Julius Hortvet presented a special paper on sublimation, which evoked considerable comment. The method he outlined gives promise of being adaptable to quantitative work and also of having wide industrial application, especially in the purification of chemicals.

The referee's report upon the preparation of neutral ammonium citrate terminates the work upon this important subject which has been before the association continuously for a period of many years. To those interested in the use of this solution the settling of this question is of the most importance, since it places a reliable colorimetric method of determination, based on physico-chemical principles, in the hands of every chemist. A special paper on the utilization by crops of potash absorbed by gels probably indicates a new phase of potash availability which may have a direct bearing upon methods used in the analysis of commercial fertilizers and potash materials.

The Committee on Editing Methods of Analysis was instructed to revise the methods of the association so that they can be voted upon at the 1923 meeting, the 1923 changes incorporated therein, the revision completed, and the book of methods available for distribution by July 1, 1924. It was further voted that a chapter on the analysis of liming materials be prepared for insertion in the Methods, and that so far as possible the methods which are already official be adopted after adapting them to the determination of liming materials as such. This compilation is to be completed and published as a part of the 1922 proceedings. The present official method for citrate-insoluble phosphoric acid in fertilizers was modified so as to be applicable to precipitated phosphates, the change consisting in the reduction of the charge from 2 g. to 1 g. The Wagner method was adopted as official for the determination of available phosphoric acid in basic slag phosphates. This is the first time that there has been an official method for this determination.

The Committee on Definition of Terms and Interpretation of Results on Fertilizers presented a list of subjects for consideration and study prior to the adoption of definitions and rulings thereon.

The chairman of the Board of Editors briefly outlined the difficulties and complications which the board has encountered, and made the highly gratifying announcement that the society is now up to date in the publication of its proceedings.

A number of resolutions were adopted, of which the following is especially noteworthy:

> *Resolved,* That this Association go on record as heartily endorsing the campaign recently inaugurated by the American Chemical Society to educate the American people to a better understanding of chemistry, its possibilities, and applications to everyday life.

The following officers were appointed for the ensuing year:

Honorary President: HARVEY W. WILEY.
President: A. J. PATTEN.
Vice President: R. E. DOOLITTLE.
Secretary-Treasurer: W. W. SKINNER.

Additional members of the Executive Committee are E. M. Bailey, P. B. Dunbar, R. W. Balcom, J. B. Weems, and J. W. Kellogg.

The names of members of committees, referees, and associate referees for the year 1923 may be secured through the secretary. The full proceedings will be printed in the *Journal of the Association of Official Agricultural Chemists.*

NOTES AND CORRESPONDENCE

An Appreciation

Editor of the Journal of Industrial and Engineering Chemistry:

On the eve of my return from New York to England, I cannot refrain from asking you to allow me, through the columns of your well-known journal, to express my thanks to all who have helped to make my visit to the United States a continuous round of pleasure, instruction, and interest. I leave more than ever impressed with the great work which is being done for the American nation by the profession and industry of chemistry, with the value of so great an organization as the AMERICAN CHEMICAL SOCIETY in the consolidation of chemical interests and the direction of their influence upon the national life; and especially with your organization, both through state action and through private and industrial enterprise, for the prosecution of research—the secret and foundation of all real progress.

To yourself, sir, and to your colleague, Dr. Charles L. Parsons, I am indebted for a welcome to Washington which I shall never forget, and for an opportunity of meeting a gathering of distinguished American scientists whom it was indeed an honor and a pleasure to know. I return, as all my fellow-delegates do, overwhelmed with the memory of American friendship and hospitality. The fundamental unity of the English-speaking race is no longer to us a mere theory but a potent reality for us and for the world, and I trust and believe that the only rivalry England and America will ever know is the rivalry as to which shall best serve the welfare and progress of mankind.

With real gratitude for all the kindness I have received on this side and with the heartiest wishes for the prosperity of your work.

F. E. HAMER
Editor, The Chemical Age

NEW YORK CITY
October 27, 1922

The Paint Industry

Editor of the Journal of Industrial and Engineering Chemistry:

To your September issue, p. 775, Dr. A. H. Sabin contributes a brief review of the progress of the paint industry, which parallels the famous chapter on "Snakes in Ireland." Dr. Sabin writes "little can be said of progress in the paint industry," and then proceeds to describe the manufacture of Titanox, its properties and qualities, with an equivocal glance at light-resistant lithopone and a recognition of Perilla Oil.

The impression left by this statement is certainly not favorable to the industry. It is hardly to be expected that in an industry so long established new materials should be discovered daily, but progress in any industry certainly does not consist merely of the introduction of new materials; rather it consists in improvements in methods and processes, in increased knowledge of materials, in better laboratory control, in better technology.

In all these fields the paint and varnish industry has made consistent progress, not only in the past year, but during a number of years past. The practical chemist, once a *rara avis*, is now an important factor in most plants. The research laboratory, once unknown in this field, is now an established feature of the larger organizations, and all of these are correlated through the Federation of Production Clubs, the Scientific Section of the Educational Bureau, and Committee D-1 of the American Society for Testing Materials.

Not only has great progress been made in the standardization of specifications for materials and products—e. g., the specifications of the Interdepartmental Committee of the Government at Washington, and the standard specifications of the A. S. T. M.—but considerable progress has been made in elucidation of the physical and physico-chemical laws underlying paint problems, together with means for measurement and numerical expression of properties and qualities.

As to lithopone, it is a fact familiar to all paint manufacturers that practically all the standard brands show decided improvement in light-resistance as well as in physical uniformity, while at least one and possibly others are—as pigments in oil—practically light-proof. Their use in exterior paints is constantly increasing, and, in contradiction to the opinion quoted by Dr. Sabin, it is the general opinion that this use will expand indefinitely.

In a long-established industry progress is commonly manifested in details rather than in revolutionary changes, and in these details both the paint and the varnish industry show encouraging progress. A reference to your own files during the past year will amply demonstrate this assertion.

G. B. HECKEL, *Secretary*

PAINT MANUFACTURERS' ASSOCIATION
OF THE UNITED STATES
PHILADELPHIA, PA.
October 9, 1922

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Editor of the Journal of Industrial and Engineering Chemistry:

Mr. Heckel's criticism is that of a hopeful optimist; but the review was an attempt to tell of facts as they are, and not what we hoped for. I, myself, know little about lithopone, for example; but I had the separate and agreeing opinions of several of the largest makers of that substance, and of chemists of paint companies that use it. I know it does not agree with the advertisements. I appreciate the value of the work done by Dr. Bingham, Mr. Green, and others, but it seems incomplete, and special mention may be deferred until some practical results are shown. If there has been any important progress in varnish making during the year, none of the makers whom I have been able to consult have heard of it. There is no use in taking space for telling of things that are not yet done.

A. H. SABIN

NATIONAL LEAD COMPANY
NEW YORK, N. Y.
October 20, 1922

A Mistaken Rumor

A rumor is spreading in this country that the International Research Council, which is represented in America by the National Research Council, took action at its meeting in Brussels last July excluding Germans and Austrians from its meetings and from meetings of the various international unions affiliated with it for a period of twelve years. No such action was proposed or taken. No German or Austrian organizations have as yet been admitted to the International Research Council but their admission is probably a matter of the near future. [VERNON KELLOGG, *Permanent Secretary.*]

A New Method of Color Measurement for Oils

Editor of the Journal of Industrial and Engineering Chemistry:

I cannot refrain from writing to straighten out, and in some cases contradict a number of statements regarding Lovibond's tintometer contained in an article headed "A New Method of Color Measurement for Oils" in your issue of April 1922, page 269.

It is evident from the start that the writers are not themselves well acquainted with Lovibond's system or Lovibond's Color Laws.

In the foreword it is implied that Lovibond's method is not consistent if we give the word "consistent" its dictionary meaning of "not contradictory," then most certainly Lovibond's method *is* consistent, as with proper precautions for the initial measurement it can be relied upon and be reproduced with accuracy in any country.

It is also stated to be unsatisfactory for three reasons. I will take them in order and as lettered:

1—WIDE SEPARATION OF THE SQUARES OF LIGHT. The wide separation of the fields is found by some color workers to be a great help, and after twenty-five years of color work, I am not at all certain it is not the correct method; but as, on the other hand, some persons have found difficulty in their readings by this method, in the newest instruments it has been abandoned and the two fields are now side by side. As yet no optical device has been approved by the Tintometer Laboratory workers as giving true and reliable color readings.

2—MATCHING OILS ABOVE 500 COLOR. Mr. Lovibond himself, as long ago as in 1901, begged chemists testing oils for color not to measure them in too great a color depth. He advised a small cell or thin film but the commercial man would not hear of it and adopted 18 in. and $5^1/_4$ in. as their standard cells.

3—COLORS NOT ADDITIVE. If your writers will refer to page 8 of Mr. Lovibond's book, "Light and Color Theories," they will find the answer to (3) in Law 9. "Every definite substance has its own specific rate of color development for regularly increasing thicknesses." This law, which is one upon which the whole science of color measurement hangs, has been overlooked throughout the paper before us.

We would like to add here that it is quite easy to determine the actual amount of coloring matter removed by fuller's earth under definite conditions by means of the tintometer. The use of the Lovibond scale for oils was first suggested by Mr. Lovibond himself, in connection with Sir Boverton Redwood. The cell then advised was $^1/_{16}$ in. strata thickness; the oil trade, however, preferred the longer length of $5^1/_4$ in., which was too great a length as, of course, the longer the length of cell the deeper is the color to be matched by the standard glasses.

The color of a solution always changes very gradually by means of a sufficiently large number of graduated cells, the color absorption curves can be accurately established, and the exact point where one color dies out and the other appears can be ascertained. Here again I would refer to "Light and Color Theories," page 33 and plate 5.

Mr. Lovibond proved many years ago that percentage dilution and cell dilution by varying thickness gave concordant results.

It would be interesting to know what is meant by "colors between 3 or 4 and 200" and "above 400°." It is impossible for any color observer to read with accuracy at such a depth as 200, or for the glass standards themselves to be made. The best way is to adopt the use of a thin film of the substance to be measured.

The relationship between the true Lovibond scale and the arbitrary scale can always be found with a little careful work.

Lovibond curves are, of course, not additive in one sense on account of the before-mentioned Law 9, but the colors themselves are additive.

With reference to the "True color" scale mentioned, it would be interesting to learn on what this scale is based and why it is "True," also of what the standards themselves consist.

THE TINTOMETER LTD.
SALISBURY, ENGLAND
June 10, 1922

F. E. BAKER

Editor of the Journal of Industrial and Engineering Chemistry:

The writers had no intention of casting any reflection upon the admirable work of Lovibond and his associates on color. They have read his book on "Light and Color Theories," and feel that Mr. Baker, if he had read our articles more carefully, would have noted a reference to many points on which he asks for information. We have carefully stated, mathematically and otherwise—although possibly in a different form—the fundamental laws of color measurement, which we are said to have overlooked.

As stated, the scope of our work was to develop a method for use in the petroleum industry, where, besides other methods, the Lovibond amber-colored glasses are now employed. Two years' personal work in both laboratory and plant, as well as conferences with other oil chemists, convinced us of many disadvantages in using the Lovibond amber-colored glasses. These disadvantages are carefully noted in our article, and it may again be emphasized that it is practically impossible to check readings by this system with dark stocks, with which our work was largely concerned, and as a consequence of this disadvantage, the yield of filtered oils often varies by many hundreds of gallons with resulting uncertainty in filtering processes.

That some form of accurate color measurement is greatly needed, is evident by the vast amount of research now under way by various oil chemists.

In our foreword, "consistent" was used in another equally rigid dictionary meaning of "uniform," as evidence of our attempt to find a method and apparatus which would measure the color of all petroleum oils from the lightest to the darkest. As stated, with the present Lovibond amber glasses, for dark oils it is imperative that these be diluted with water-white kerosene or other solvent to permit them to be matched in the tintometer. Furthermore, the values so obtained on dilution bear no definite relation to the colors of lighter undiluted oils.

Regarding "wide separation of light squares," the writers believe that most color experts will agree that close juxtaposition of color squares is a great aid in matching. Mr. Baker admits a difference of opinions, yet states that no optical device has been approved by his laboratory. Other methods have, however, been found.

In matching oils above 500 color, we are in apparent agreement with Lovibond's original suggestion of measuring oils in thin films. We have devised such thin films and applied them successfully to the problem in hand.

In our adaptation of thin films, according to Mr. Baker, we also check Lovibond's original observation regarding the relation between percentage dilution and cell dilution by varying thickness.

Again referring to our article, by "colors between 3 or 4 and 200," is meant the color of the Lovibond amber glasses. Use of any tri- or multi-colored standards would obviously be impracticable in an oil-testing laboratory where speed and simplicity of recording data are both imperative. Mr. Baker again agrees with our data in saying that it is better to measure thin films than to use a dark color glass.

Our "True color," as stated, means a figure proportional to the amount of coloring matter present in the oil. The relation between the Lovibond color and True color is clearly explained in detail and given in tabular form where the relation between N. P. A. colors, Lovibond colors (Series 500), and True color values is stated. Detailed curves, Plate VIII and Plate IX, also give plotted data showing these relationships. Reference to these plates indicates that Lovibond color and True color are the same up to 50°, but deviate above this point. In fact, we refer to standardizing our oil standard, L. S., against a 50 Lovibond glass.

In conclusion, it may be stated that we do not claim any new system, but rather an adaptation of the laws and facts of color measurement to a method for measuring the true colors of petroleum oil from the lightest to the darkest, using specially constructed thin films for measuring the darker oils. Research and plant work, involving oil varying in amount from 1 cc. to 8000 gal., has been covered, and data obtained on a laboratory scale have been checked absolutely in the plant, all being based on our True color method. Plant control was compared, incidentally, by both Lovibond and True colors.

It is regretted that Mr. Baker interpreted our article as reflecting on Lovibond's basic laws, and pioneer work in this field. A more careful perusal of our description and data indicates the various points involved.

LEON W. PARSONS

RESEARCH LABORATORY OF APPLIED CHEMISTRY
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
CAMBRIDGE, MASS.
October 30, 1922

The Plant Manager and the Chemist

Editor of the Journal of Industrial and Engineering Chemistry:

Mr. Griffin's comment in the October issue of THIS JOURNAL, on the article entitled, "The Plant Manager and the Chemist," embodies several points of extreme interest to both the chemist and the plant manager.

Mr. Griffin maintains that the chemist who does not require authority to secure the coöperative development of his ideas would be discredited for holding a subordinate position. This is admittedly true, but it is equally true that the chemist does not wish to stay in a subordinate position, nor is it to the advantage of the plant to keep him in such a place.

Mr. Griffin's comment that he has seen many plant managers who are out of place, is undoubtedly true, as many men in this position have the position for reasons other than their adaptability to it, the position being given to them for a great many reasons that are present in all industrial plants. Invariably, however, the plant manager has to engage the chemists for the plant, and for this reason the chemist must, until there is some other way of selecting plant managers, accept them as such.

It is to be remembered that the average plant chemist, in comparison with the plant manager, is a new-comer, most managers only attaining their position after long experience in their particular branch of manufacture. The technical man must learn to take advantage of the experience accumulated by the men who have long been connected with the industry and must be guided in his work largely by such experience.

Many men engage themselves as chemists who believe that they are in direct line for executive positions and that these positions should come quickly. If the advances do not realize with speed, then many chemists feel that their case is not treated fairly and that the profession as a whole is not properly recognized. I believe in the natural evolution of an industrial chemist, which is to become a manager of the industry. I do not mean the plant manager alone, but there is no reason why he should not manage the whole of the undertaking. His training should fit him to be a keen, observing man of business.

There are plenty of illustrations where this has been the result with chemists who were fitted to their work and who wanted to get the most out of it. It is a fact that many chemists are offered the pay of ordinary employees when their training warrants a very much better return. There is not at this time any way of correcting this difficulty. It is certain, however, that a chemist cannot be good in his work and be hired for a niggardly sum for long, so that a chemist making a good showing is bound to have the returns somewhere near what they should be.

Many managers expect more from inexperienced chemists than it would be possible for experienced men to deliver, and I believe that this condition will continue until the trained chemist is more fully established in industrial plants. Then there will be a medium of understanding with the chemist, plant manager, and the embryo chemist looking for honors in production.

I acknowledge the fact that the chemists as a whole are constant and hardworking, but I am of the opinion that there are a vast number of men in the profession who are indifferent to the fine points in it and who are as a result injuring high-grade chemists. The title of chemist should indicate that the holder is a person of considerable mental attainments.

It was farthest from my intentions not to show a "kindly sympathetic spirit of encouragement." Chemists should assume greater responsibility and interest in the manufacture than they do at present, as the future of any industrial firm should lie in the improvement of its products through the intelligent application of technical ideas.

GEORGE L. O'BRIEN

O'BRIEN VARNISH COMPANY
SOUTH BEND, IND.
November 9, 1922

"America First"

Editor of the Journal of Industrial and Engineering Chemistry:

Two very different tendencies have grown in the world during and since the war. During the war, more than a dozen nations fought together in close coöperation under a single command. American soldiers used French airplanes and French artillery. Without them the contribution of America to the war would have been almost negligible. Thousands of Americans worked for the Government on the "dollar-a-year" basis and most of these were not profiteers. The American people ate corn bread and curtailed their use of sugar, that the people of England and France might not starve. Fighting against us were four other nations, equally united. On both sides workmen forgot their grievances and worked for the common cause, and in return received more consideration and more adequate pay.

Since the war, nationalistic and capitalistic tendencies have become more pronounced and more harmful than ever before. "America First" has become so exactly like "Deutschland über Alles" that it is hard to distinguish the spirit of the two slogans, though *both* slogans are also used in the sense of a patriotic international rivalry with no thought of injury to others. Instead of establishing national boundaries on economic principles and for the common welfare, the lines were placed largely for strategic reasons, as though war were to be the common and normal condition of the world.

All Europe was preparing for decades for the catastrophe of 1914. Instead of realizing that every nation was responsible in part for the conditions that had arisen, and uniting now in their common misery to repair the injury that has been done, too many statesmen are intent on some selfish aim for their own people, apparently indifferent to the injury they are doing to other nations. Frenchmen insist that Germany alone was responsible for the war and fought to destroy France and secure dominion over Europe and ultimately over the world. Germans are equally insistent that they fought a defensive war against an overwhelming combination. The intellectual leaders of

France refuse to have any intercourse or acquaintance with the intellectual leaders of Germany, and suspicion and hatred grow fast on both sides. French statesmen insist on the full payment of the so-called reparations, which are really, in part, indemnities to provide pensions in France and England. They seem to be rather glad that this insistence is bringing economic ruin to Germany, and to forget that it may make further payments impossible for years to come. And it is not certain that Germans and especially German capitalists are doing all that they might to comply with the terms of the treaty.

Before the war, it was customary to travel all over Western Europe without a passport. Now, following the example set by America, expensive visés are required, passports are examined at every boundary, and customs examinations are a nightmare to travelers. An exaggerated spirit of nationalism holds sway everywhere.

No one who has visited Europe recently and who has seen at all below the surface will claim that the picture is too dark. Indeed, one prominent German chemist with whom I talked this summer sees starvation and cannibalism coming to Germany as they have come to Russia. And no one seems to see any way out.

Yet, the way is clear before us if the nations could only take the lessons of history and apply them. It is only a little more than fifty years since Prussia and Bavaria fought each other, but very soon afterwards Bismarck had welded Prussia, Bavaria, and the other German states into a unified empire,—with the fatal mistake, however, that the unification grew out of successful wars and was essentially military at its foundations. Instead of being a federation of states with equal rights, the Prussian State was dominant. In 1914 *some* Germans—though by no means *all*—wished to build an enlarged Germany and make their empire dominant in Europe. Instead of an empire of that sort, it should be clear to every one that further wars between France and Germany must bring a hundred- or a thousand-fold greater loss to *each* than the small gain which might possibly come to the victor in the strife. Switzerland is a federal state, including Frenchmen, Germans, and Italians. The only reasons why France and Germany may not also form a federal state seem to be their larger size and the animosities which have grown from centuries of intermittent war. These reasons are doubtless too great to be overcome at once, but France and Germany should certainly find some practicable way to coöperate in the restoration of the devasted areas on a basis that will not bring financial ruin to Germany or make necessary the maintenance of a large and expensive army in France.

It will be asked why such questions should be discussed in a chemical journal. Because the chemists and other scientific men may, if they will, contribute very much toward a better understanding between France and Germany. The International Union of Pure and Applied Chemistry excludes Germans and Austrians from membership, apparently on the basis that the allies were on so much higher a plane during the war that they are unwilling to associate with them. Have the events of the last four years demonstrated that Frenchmen and Englishmen and Americans are so far less selfish than Germans and Austrians in their national ambitions that they can afford to take a "holier-than-thou" attitude? And, even if we still believe that some Germans were very wrong in their Pan-Germanism, is there more hope that the Germany of the future will become a safe member of international society if she is ostracized than there would be if we met her scientific men on the basis of equality and friendly coöperation?

When the French soldiers came to the Rhine they found the German children starving, and they fed them. The French *poilus* and the German common people learned a lesson in human brotherhood which will not soon be forgotten. It has long been the custom of the scientific men of the world to work together in friendly rivalry, and to share their discoveries freely with each other. Is it not possible, now, for the chemists of the world to meet together once more and to contribute their share toward the establishment of genuine peace among the nations?

W. A. NOYES

UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS
November 1, 1922

Frank Sherman Washburn

A man of broad, driving interest was Frank Sherman Washburn—a man of personal power, who never knew when to stop. From the beginning of his career he drove himself to the limit of his physical endurance, and up to the time of his death, on October 9, he continued driving himself. Even in periods of rest he held himself to a rigid schedule in everything.

FRANK SHERMAN WASHBURN

The American Cyanamid Company stands as a memorial to the force of his character and his ability to associate able men with him in his enterprises. Never overbearing, yet always forceful, he made associations with men of the highest type in carrying through his many ideas. As a tribute to his ability as an organizer, he was appointed to carry through the immense government fixed nitrogen project at Muscle Shoals, and, working against the almost insurmountable difficulties of the war-time pressure, he had this plant producing fixed nitrogen within a year from the signing of the contract. The feat was accomplished only with the utmost sacrifice of his personal energy. Never a moment of time was wasted and never a bit of his limitless supply of energy was allowed to be misdirected. Probably the strain of the investigation of his conduct of this project, which followed the war, had more to do with the final failure of his physique than any other one thing.

As a friend and companion, few could equal him. His broad interest in affairs and the immense fund of information in his well-ordered mind made him a delightful talker; yet as a listener he had a most charming deference to the opinions of others. His character may well be read in the characters of those with whom he associated. His hobbies, if such a dynamic person may be considered to have hobbies, were education and boating. His educational work included the chairmanship of the drive for an endowment for Cornell University, of which he was trustee for many years. On his infrequent boating trips he always played with the same whole-hearted energy that he displayed in his business.

It will be long before another comes to fill his place.

The Nobel Prize in Chemistry for 1921 has been awarded to Frederick Soddy, professor of inorganic and physical chemistry at the University of Oxford. Professor Soddy was from 1900 to 1902 demonstrator in chemistry at McGill University, Montreal. The prize for 1922 has been awarded to Francis William Aston, research fellow at Trinity College, Cambridge. Dr. Aston recently delivered a very interesting series of lectures on isotopes in this country.

WASHINGTON NOTES

As usual, the past month brought to Washington several conventions of interest to the chemist. From October 25 to 28 the Optical Society of America held its 7th annual convention and exhibit of optical instruments at the Bureau of Standards. Then came the meeting of the Association of Feed Control Officials, at the Raleigh Hotel on November 13 and 14. The dominant note sounded at this meeting was uniformity as to labels and application blanks. Some twenty-one states were represented, and the opinion was practically unanimous that the types of uniform labels and registration blanks submitted could, with few exceptions, be accepted in all the states having feed control laws. This action has been taken after several years' efforts on the part of the officials of the association. Other important business accomplished was the adoption as official of tentative standards on crude fiber, standard middlings, flour middlings, and red dog flour. Next came the annual meeting of the Association of Official Agricultural Chemists, reported elsewhere in This Journal. That convention had scarcely completed its deliberations when the American Society of Milling and Baking Technology convened at the Raleigh Hotel and voted to amalgamate with the American Association of Cereal Chemists. The officers of the society were reëlected, and it was decided to maintain the present organization until the American Association of Cereal Chemists meets next June and acts upon the resolution to combine. And now, as we go to press, the Association of Land Grant Colleges is about to hold its 36th annual convention at the New Willard Hotel.

Tariff Developments

Every effort is being made by the Government to facilitate the operation of the 1922 Tariff Act. An Executive Order has been issued declaring that all requests for action or relief under the Tariff Act shall be filed with the Tariff Commission. The latter, in turn, has issued regulations stressing the importance of the following points: Applications for investigation are not required to be in any special form. All that is necessary is a simple statement of the relief sought and the grounds therefor. No investigation will be ordered except for good and sufficient reason. The commission will not confine itself to the issues presented but will modify them as seems best. All evidence presented will be subject to verification.

Assistant Secretary of the Treasury Clifford has issued a formula to guide appraising officers in assessing duties on noncompetitive coal-tar products. This is in contradistinction to American valuation which is to be applied to duties on competitive coal-tar products. It is hoped that the application of this formula will result in uniform tariff duties at all ports.

Meantime a conference of representatives of the Tariff Commission, the Bureau of Standards, and the Customs Division of the Treasury Department, was held in New York, November 2 and 3, to discuss the administration of the coal-tar provisions of the new tariff law. Another conference is scheduled for early in December, and it is probable that similar conferences will be held from time to time. Just now these representatives are most concerned with plans for determining the standard strength of dyes in commercial use prior to July 1, 1914, and securing domestic samples for comparative purposes.

The flexible section of the McCumber-Fordney Tariff Act has been in operation since November 9, and about fifteen applications for revisions of duty on chemical products have been received by the Tariff Commission, some asking for increases in duty and others for decreases. One case of chemicals is now before the commissioners for action, and it is probable that by the time This Journal issues a preliminary investigation will have been ordered. This will be the first chemical case to be investigated under the new law.

Conference on Lubricating Oils

Proposed changes in the classification of lubricating oil specifications were discussed at a joint meeting of the Interdepartmental Petroleum Specifications Committee, the Advisory Board to the Committee, the Lubricants Division of the Society of Automotive Engineers, and the Technical Advisory Committee of the American Petroleum Institute, held in Washington, D. C., on November 13.

Separate schemes for classification were presented by representatives of the Society of Automotive Engineers and by the Navy Department. After considerable discussion, it was brought out that a difference exists between turbine oils for land service and turbine oils for marine service; also that, for turbine oils with paraffin base and asphalt base, lubricants seem to have the same effective viscosity at about 130° F.

A special committee was appointed to consider a list of descriptive names to be used for lubricating oils in the Federal specifications, for explanatory purposes only, and this committee reported a majority opinion that four names should be used together with descriptive numbers: light oil, to cover S. A. E. Nos. 15 and 20; medium oil to cover Nos. 30 and 40; heavy oil to cover No. 50; extra heavy oil to cover Nos. 60, 80, 95, and 115. This majority report was accepted. A minority report, which follows the present classification adopted by the Navy Department, was also submitted.

The conference recommended the measurement of viscosities of oils up to 500 series at 100° F., 600 series and higher at 210° F.

It was further decided to request the Interdepartmental Committee to omit requirement for organic acidity from all motor oil specifications; to make investigations into the relation between acidity, emulsion tests, and service tests, and into the relation between oxidation and evaporation and service tests.

The conference also discussed color, carbon residue, and pourtest requirements for lubricating oils and the fire point for mineral seal oil. The Interdepartmental Committee is considering taking all these proposals, and will take decisive action at a later meeting.

Agricultural Research Journal to Resume

The United States Department of Agriculture, in coöperation with the Association of Land Grant Colleges, will resume the publication of *The Journal of Agricultural Research*, which, with a number of other publications issued by executive branches of the Government, was discontinued over a year ago. The first issue is expected to appear January 6, 1923.

This journal was established in 1913 for the purpose of segregating and rendering more generally available to agricultural specialists the reports of important discoveries or other original investigations of interest to agriculture.

Washington Chemical Society Officers

The Washington Section of the American Chemical Society on November 9 elected the following officers for 1923:

President: W. M. Clark.

Secretary: J. B. Reed.

Treasurer: H. W. Houghton.

Councilors: W. D. Collins, R. B. Sosman, W. W. Skinner, F. C. Cook and R. C. Wells.

Executive Committee: L. H. Adams, R. O. E. Davis, V. K. Chesnut, C. W. Bacon, A. Seidell, E. T. Wherry, and F. W. Smither.

Interdepartmental Patent Board at Washington

By Executive Order an Interdepartmental Patent Board has been created consisting of the following members:

Dr. Andrew Stewart, Department of the Interior, *Chairman.*
Lt. Col. Joseph I. McMullen, War Department, *Secretary.*
Dr. F. G. Cottrell, Department of Agriculture.
Mr. Harry E. Knight, Department of Justice.
Dr. S. W. Stratton, Department of Commerce.

The researches which the board will conduct relate to the status of inventions and patents of employees of the Government as well as to the administration of patents and patent rights owned by the Government. The board is assembling data preliminary to recommending to the President, for his consideration and approval, a policy to be followed by the Government in the premises, the need for such a policy having been made increasingly manifest during the past several years.

The board will also act as a center for the dissemination of information among the several governmental departments and other units relating to patents and patent rights owned by the Government.

The President has announced that the resignation of Dr. George Otis Smith as director of the United States Geological Survey is of a temporary nature, and that he will be reappointed to his former position when his work with the Federal Coal Fact Finding Commission has been completed.

Frederick S. Dickson, former chief of the dye and chemical control section of the Treasury Department, has been retained by the State Department in an advisory capacity.

November 18, 1922

PARIS LETTER

By Charles Lormand, 4 Avenue de l'Observatoire, Paris, France

International Congress of Combustible Liquids

The importance of combustible liquids in the life of a country was demonstrated by the necessities of war. When Germany was cut off from oil supplies because of the blockade, she directed her research to the transformation of coal into combustible liquids, and—thanks to the success of these investigations—she was able to keep her airplanes, automobiles, and tanks supplied.

In France, the consumption of combustible liquids is 8,000,000 hectoliters a year. At the International Congress and Exposition of Combustible Liquids, held at Paris in the early part of October, under the presidency of Mr. Sabatier, an inventory was made of all the possible resources of combustible liquids and their utilization.

As Mr. Berthelot said in the opening conference, humanity is acting in regard to combustibles like a son who is squandering the family fortune. We waste without thought that which is not inexhaustible; and, as Sir William Pope suggested a year ago, ought we not to hunt for combustibles in the vegetable products which have made available through photosynthesis, resources which will exist as long as the sun lights the world; and should not the efforts of chemistry be directed toward searching for an imitation of the mechanism of the vegetable world? Water, oxygen, carbon dioxide are able by a catalytic process to produce carbohydrates, and from them the oily materials of which combustion closes the cycle.

The Congress was divided into six Sections:

Section of Petroleum—Here the methods of exploitation by subterranean drainage were studied—such as are in practice at Pechelbronn, under the direction of Mr. de Chambrier. The members of the Congress were able to visit this exploitation.

I would also call attention to the process described by Mr. Maihle, which consists of transforming solid hydrocarbons or those with a high boiling point to liquid hydrocarbons that are very volatile. The method of "cracking" of Burton, used in the United States, gives efficiencies of 30 to 40 per cent, but has the inconvenience of operating under pressure.

The catalytic decomposition of these hydrocarbons can be effected in the presence of catalysts, such as copper or iron. The products obtained vary from a gas with calorific value of 15,000 calories, to an oil boiling at a maximum of 200° C.

The hydrogenation processes were likewise studied, and especially the Bergius process, which hydrogenizes, at a pressure of 200 atmospheres and 400° C., the formerly nonutilizable residues, such as the heavy oils, tars, asphalts; even coal has been hydrogenated to give useful hydrocarbons.

All the hydrogenation processes should be carefully perfected, for they are very often applicable only in very narrow limits of temperature. This fact has, moreover, already been pointed out by Sabatier—it is possible at high temperatures to obtain a product that is incompletely hydrogenated, while at a lower temperature a completely hydrogenated product is obtained. An example of this is naphthalene, which at 200° C. gives a tetrahydride, and at 175° C. gives the decahydride, the pressures being identical.

The methods of using the petroleum and the processes of lubrication were also discussed.

Section of Schists—The geographic distribution of schists, both in France and in the surrounding countries, was discussed, as well as the models of furnaces for their distillation.

Section of Lignites and Peats—Statistics on the resources of lignite and peat were furnished, and the methods of their utilization. The total production of lignite in France in 1920 was 960,000 tons. The French lignites give a minimum of 15 per cent crude oil, of which 25 per cent of light oil, such as benzol, can be extracted.

Section of Benzols and Tars—The production of benzol in each country was considered, as well as the low temperature distillation of coal. The methods for recovery of the by-products, especially the removal of benzene, in the small gas factories so numerous in France were discussed, also the hydrogenation of tar products, and the by-products of the manufacture of cyclohexanol and tetralin.

A Committee on International Terminology has been formed, composed of a representative of each country, to make more uniform the use of terms which often give rise to confusion—for example, the words "benzene," "benzol," "benzine," often used interchangeably.

Section of Alcohol—France is, indeed, an agricultural country, a great producer of alcohol, and she should find in this alcohol a valuable fuel. I mentioned once before the "Concours du Carburant National," and the results which it has accomplished.

Aside from the alcohol produced from beets and artichokes, the manufacture of alcohol from the cellulose of wood was recommended. The attempts of the Forest Products Laboratory of Madison, Wis., were mentioned. The Prodor process was described in detail. In this process the cellulose is treated with hydrochloric acid concentrated in the cold; thus, there is no destruction of glucose during the operation, as when hot acid is used. The efficiency obtained is about 250 liters of 100 per cent alcohol per ton of dry sawdust. There is in addition a residue consisting of pentoses, the dry distillation of which gives methanol. The equipment for this manufacture should be especially studied, and a new concrete that is not attacked by hydrochloric acid must be found out of which to make this equipment.

As the results of the Concours du Carburant National have shown, there is considerable interest in obtaining an absolute alcohol. Two solutions of this problem have been recommended: One consists in passing alcohol vapors into the rectifier over a column filled with lime; the consumption per hectoliter of alcohol is from 30 to 35 kg. of lime; this industry should have a place in factories where sugar is made and where lime is employed. Another process of dehydration consists in passing alcohol vapors over glycerol, either pure or added to potassium carbonate, calcium chloride, or potassium acetate. Under these conditions the dehydration is complete and gives a 100 per cent alcohol which can be used in a mixture with oil in proportion up to one-tenth. The Parisian busses now consume 20,000 hectoliters per month of the alcohol-benzene mixture.

One of the most curious communications made in this Section was that of Mr. Damiens and Mr. Loisy, who have been studying the gases from coke furnaces; these gases contain ethylene. They have taken the old reaction of Berthelot and tried to transform this ethylene into alcohol, accomplishing this by the use of catalysts. The one which gives the best efficiency is the oxide of copper which in the presence of sulfuric acid gives the subsulfate.

They have studied the factor of concentration of sulfuric acid and shown that a water content of 2 per cent decreases most the absorption speed of ethylene by the sulfuric acid. They have also shown that the optimum temperature for this absorption is 60° C. But the most interesting thing about this absorption mechanism is that when working in the cold, they obtain an ethyl sulfuric acid, which on hydrolysis gives alcohol. On the other hand, with high temperature, they obtain no longer an oxygenated product, but a polymerization of the ethylene, and the final product obtained consists of an oil of a density of 0.77 and a boiling point of 110° C.

This process, which permits obtaining either alcohol or oil, is not only a laboratory process. It has been the object of industrial attempts on a large scale, which have shown good operation.

Section of Vegetable Oils—Mr. Maihle developed his method of hydrogenation of vegetable and animal oils, which makes possible the transformation of these oils in petroleums.

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This very interesting Congress was completed by the Exposition where all the engines using combustible liquids were shown in operation, and especially the engines of the Powders Service, using all the recommended mixtures successively, as well as the motors of mazout of the Inventions Service, where the mazout is first distilled and the gases of distillation are burned. We were able to compare this process with that using the pulverization of mazout and its entrainment through a current of air.

The visits to the factories in the vicinity of Paris, in Alsace-Lorraine, and in the Sarre region, ended the meeting of the Congress.

October 31, 1922

LONDON LETTER

By Hugh Griffiths, 15 New Bridge St., London, E. C. 4, England

Low Temperature Research

An encouraging new feature in meetings of scientific societies is the joint discussion held by several societies. It is realized that this kind of coöperation covers overlapping fringes of activity, and new points of view are presented which are stimulating to the specialist members who are liable to get narrow views.

An interesting joint meeting of the Faraday Society and the British Cold Storage and Ice Association has just been held. The physical papers included contributions from Dr. Onnes of Leyden, who has succeeded in reaching within less than one degree of absolute zero. Dr. Crommelin gave a detailed description of the apparatus employed for research work at Leyden, which is well worth the attention of all makers in research on liquefied gases and gases at low temperatures.

The technical papers included a full discussion of modern methods of manufacturing oxygen by K. S. Murray of the British Oxygen Co. Ltd., a paper on hydrogen manufacture by G. Claude,[1] and a paper on heat insulation materials by Dr. Ezer Griffiths.

The information given by Mr. Murray was largely new and very complete, and the somewhat surprising information was given, that actual experience with various systems had shown that the product of 1000 cu. ft. of oxygen of 98.5 per cent purity required not less than 30 to 33 b. h. p. hours. It was also mentioned that while oxygen had been employed in the chemical industry in Germany in the production of nitric and acetic acids, the use of oxygen for chemical purposes was really in its infancy, and the opinion was expressed that future development of oxgyen as a raw material for chemical manufacturers was certain.

Dr. Claude's paper, as would be expected, had special reference to synthetic ammonia, and the system of hydrogen production discussed is that at present used at Grande Paroisse. The process consists of liquefying the carbon monoxide from water gas, etc., under a pressure of 200 to 450 lbs. per sq. in.

It was rather disappointing to find that the purely chemical applications of refrigeration were not discussed, particularly as in England many processes involving the use of refrigeration have recently been devised. The problem of "niter cake" is always with us, and there are some who believe that the only solution will be found in freezing out Glauber's salt from a solution of this product. The application of refrigeration in the manufacture of perfume ingredients from essential oils is fairly extensive, but the methods usually employed are primitive, and the plants somewhat crude.

Hydronaphthalenes

Since the war, attention has been directed toward Rodleben, where there is a plant capable of producing about 100 tons per day of hydrogenated naphthalenes. During the war this installation produced a substitute for turpentine, and the naphthalene derivatives were employed as solvents for synthetic resins of the bakelite type.

The tetrahydro- and decahydronaphthalenes are not difficult to manufacture, and they have been proposed as substitutes for turpentine. A recent investigation carried out by Coleman and Bilham for the Department of Scientific and Industrial Research gives some definite information regarding these products. The report of these investigations deals chiefly with "Dekalin," which is a mixture containing about 80 per cent decahydronaphthalene and 20 per cent tetrahydronaphthalene. In physical properties this mixture is similar to turpentine, but is less volatile and less viscous, and has a somewhat higher flush point. Dekalin and various similar materials have come into use in Germany in the paint and varnish industry, and it appears from the report of Coleman and Bilham that the new materials are actually better than turpentine. They possess in common with turpentine the property of acting as oxygen carriers, therefore inducing autoxidation of the drying constituents of a paint or varnish.

Colloid Chemistry

The study of technical problems by the methods of colloid chemistry is becoming very fashionable, and this method has recently been sanctioned in England by government support. Volumes dealing with the application of colloid chemistry to industrial matters are now issued yearly through H. M. Stationery Office by the Department of Scientific and Industrial Research.

This year the fourth report has appeared, and is much more comprehensive and bulky than the previous issues. An extra volume has also been published from the same source, containing a record of the discussion held jointly by the Faraday Society and the Physical Society. These volumes contain some excellent information on the application of colloid theories to a long range of industrial problems.

The flotation process comes in for very full treatment, and soap boiling, steel, rubber, glass, lubricants, and colloid fuels are all considered. The papers on the theory of the flotation process by Edwin Edser are of exceptional merit. There is also included in the first report a paper on catalytic hydrogenation by E. F. Armstrong and T. P. Hilditch.

One usually feels in reading the literature of colloid chemistry that the explanations frequently given are merely translations of ideas into words, and that the state of knowledge is very indefinite. The volumes mentioned are singularly free from this defect, and most of the papers show serious endeavor to treat colloidal problems in a strictly physical and scientific manner.

October 23, 1922

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[1] See page 1118 of this issue

Canadian Chemical Production Well Maintained

The gross value of chemicals and allied products manufactured in Canada in 1920 was approximately $122,000,000, according to a report published from the Dominion Bureau of Statistics at Ottawa.

The report states that the actual capital invested in the 456 plants operating in this group of industries in 1920 was $120,000,000. Pigments, paints, and varnishes made in 48 plants were valued at $27,000,000. The report covers ten principal industries producing, respectively, coal tar and its products; acids, alkalies, salts, and compressed gases; explosives, ammunition, fireworks, and matches; fertilizers; medicinal and pharmaceutical preparations; paints, pigments, and varnishes; soap, perfumery, cosmetics, and toilet preparations; inks, dyes, and colors; wood distillates and extracts; miscellaneous chemicals.

The imports of chemicals and allied products into Canada have gradually increased from $3,469,000 in 1895 to $24,000,000 in the twelve months ending March 1922. The exports of Canadian products of the same class have risen from $760,000 in 1892 to $9,000,000 in the twelve months ending March of the present year. During the war the great production of explosives in Canada and the shipment of this commodity to the war zone raised the Canadian exports of chemical products to a grand total of $57,000,000 in the twelve months ending March 1919. The present export figures show that much of the advantage gained in the war-time development has been retained, and the fact that the summary statistics for the calendar year 1921 showed that 444 plants were in operation as compared with 456 in the preceding year is further evidence that the chemical industries of Canada are more than holding their own.

Interesting data on the comparative values and compositions of beet and cane molasses have been reported in the *Journal of the Society of Chemical Industry*. The following table shows the results:

	Water	Ash	Albuminoids	Carbohydrates
Cuban cane	21.12	6.65	4.68	67.55
English refinery cane	24.20	6.07	1.50	68.23
German beet	23.84	9.60	9.57	56.99
American beet	21.00	12.17	...	66.83
English refinery beet	20.00	10.00	...	70.00

Beet had a high ash and nitrogen content and nearly half of its sugar was invert. Cane molasses was found preferable for feeding purposes.

JAPAN LETTER

By K. Kashima, 1125 Ikebukuro, near Tokyo, Japan

New Patent Laws

The Patent Bureau has recently been enlarged and the patent laws have been revised. The following important improvements were made:

1—A patent should be granted to its inventor, but the true inventor is often difficult to find. A patent is granted to the first applicant, and therefore when an invention is complete patent application should be made promptly. (Art. 8)

2—An application shall be made public before the patent is granted, to give opportunity for objections or protests. (Art. 73 and 74)

3—In order to avoid misunderstanding between examiner and applicant, reasons for rejections of applications shall be shown to the applicant so that he may have opportunity to answer the objections.

4—Formerly the final decision was made by the Patent Bureau, but by the new law the applicant can ask for a second judgment and can also appeal to the Supreme Court for a final decision. (Art. 115)

5—Inventions promote the welfare of the public, and the rights should be given the inventor, even though the invention is made while he is in the service of an employer. If the employer wishes patent rights on the invention, he must pay the inventor.

6—Under the old law an examination for validity of a patent could be requested at any time during the continuation of the right. Now, validity cannot be questioned after five years from the date of the grant. (Art. 85)

7—In order to protect industry, a working clause has been inserted in the patent law. (Art. 41)

Pulp Industry

The pulp industry in this country made rapid progress during the war, but in 1921 there was a decrease in the number of factories and companies, owing to bad economic conditions. The production of pulp in this year, however, was 250,027 tons, compared with that of previous years, which was as follows:

Year	Tons
1917	169,039
1918	198,596
1919	235,227
1920	268,261

It is expected that the production in this year will show an increase of about 30 per cent, or a total of about 326,285 tons. After 1923 probably one-half of the total wood for pulp will be obtained from Kabafuto.

The imports and exports of pulp and the total amount produced during the past few years are as follows:

Year	Imports Tons	Exports Tons	Total Amount Produced
1917	14,334	3,722	
1918	28,769	3,908	223,457
1919	40,581	1,106	274.702
1920	46,808	8,180	306,889
1921	38,765	1,133	287,659

Imports of pulp are mainly from Canada and Sweden, the former aiming to sell in the Orient only. Owing to the high price of woods and wages, the cost of the domestic product is slightly higher than that of the Canadian product. A new company with a capital of 3,000,000 yen has recently been established with a view to shutting out the imported product.

The import tax of pulp in this country is now 0.2 sen per pound. As the pulp industry has developed, the Treasury Department is trying to exclude the import tax, but the directors of the paper companies are now opposing it.

September 12, 1922

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Vitamin A

At the September regular meeting of the Chemical Society of Japan, Dr. K. Takahashi, of the Agricultural Department of the Tokyo Imperial University, presented an interesting report on the nature of vitamin A. About ten years ago, Dr. M. Suzuki, of the same department, reported oryzanine as vitamin B, and since that time researches on the nature of the other three vitamins have been conducted. Dr. Takahashi has succeeded in determining the nature of vitamin A.

Rats and pigeons were bred with meals prepared from 75 per cent protein, 25 per cent butter, and a small quantity of purified oryzanine, and from 75 per cent butter, 25 per cent protein, and a small quantity of the same vitamin. They grew rapidly and were well nourished. From these results it is evident that animals can grow without carbohydrates. They were then fed with meals that contained no fat but contained vitamin A, and they all showed normal growth. It must, therefore, be concluded that carbohydrates and fats in animals' meals can be replaced to some extent by proteins.

Cod-liver oil has been shown to be rich in nutritive value, which is mainly due to the presence of vitamins. Dr. Suzuki claims that he has succeeded in isolating 1 g. of almost pure vitamin A from 1000 g. of cod-liver oil, 0.0001 g. of which has proved to be effective for recovering the health of an animal dying from insufficient nutrition.

Vitamin A, isolated by Dr. Suzuki, is a light brown liquid and soluble in almost all organic solvents, giving a yellow to yellowish red solution. By adding concentrated sulfuric acid to its chloroform solution, a deep green color develops, a reaction occurring in tests for cod-liver oil. The same solution gives a green color with Japanese acid clay. It has a reducing action, reducing silver nitrate. Vitamin A is very easily destroyed by air and light, its oxidized product having a peculiar odor. It is, however, stable in alcohol, ether, and fatty acids. It is a substance like cholesterol, probably an aldehydic compound since it contains no nitrogen. It may be practically used in olive oil solution, which will have more than a hundred times the nutritive value of butter. The detailed report will appear in the *Journal of the Chemical Society of Japan.*

The Metric System

Japan has always had a measuring system of her own. It was, however, systematically revised in the early part of the Meiji Era, so that it resembled the metric system, as the old system was very irregular. Now, however, the metric system is generally adopted in the scientific world, and the English system in industrial circles. The adoption of the metric system has at last been approved by the 44th Diet, and the Agricultural and Commercial Departments are now awaiting the enactment of the Imperial Ordinance for its adoption. It will probably be in force from January or April 1923. It is expected that the system will be described in the textbooks of schools after three years; government offices and large companies ought to adopt the system after five years, and complete adoption in general daily life should occur after twenty years.

October 11, 1922

Chandler Foundation Lecturer

Friends of Professor Chandler presented in 1910 to the trustees of Columbia University a sum of money which constitutes the Charles Frederick Chandler Foundation. The income from this fund is used to provide a lecture by an eminent chemist and to provide a medal to be presented to the lecturer in further recognition of his achievements in science. Previous lecturers on this foundation were L. H. Baekeland, Sc.D., W. F. Hillebrand, Ph.D., W. R. Whitney, Ph.D., F. Gowland Hopkins, Ph.D., and Edgar F. Smith, Ph.D.

The lecturer this winter will be Robert E. Swain, professor and head of the Department of Chemistry, Stanford University, Stanford, Calif.

Dr. Swain's subject will be "Atmospheric Pollution by Industrial Wastes." The lecture will be in Havemeyer Hall, Columbia University, on January 9, 1923, at 8:15 P.M.

List of Periodicals

A revised list of the periodicals abstracted by *Chemical Abstracts* was printed in the October 20 number of that journal. Reprints of this list may be obtained from the editor, E. J. Crane, Ohio State University, Columbus, Ohio, at 25 cents per copy.

Personals

The committee in charge of the annual award of the Perkin Medal has selected **Dr. M. C. Whitaker** as the recipient for 1923. The presentation will be made January 12, 1923, at a meeting of the American Section of the Society of Chemical Industry.

Mr. Lloyd A. Hall, formerly chief chemist of John Morrell & Co., Ottumwa, Ia., has for the past year been general manager of The Chicago Chemical Products Co., manufacturers of coal-tar dips and disinfectants.

Dr. Richard C. Lord, at one time instructor at Washington and Lee University and later engaged in industrial chemistry, has been elected assistant professor of chemistry and physics at Kenyon College, Gambier, Ohio.

Dr. James C. Andrews has severed his connection with E. I. du Pont de Nemours & Co., and is teaching physiological chemistry in the Medical School of the University of Pennsylvania.

Dr. George Barsky, formerly a research assistant of Prof. R. H. McKee, Department of Chemical Engineering, Columbia University, has been appointed to a position in the research department of the Abitibi Paper Co., Abitibi, Ont.

Mr. Leonidas R. Littleton has resigned his position as chemist with the National Aniline & Chemical Company and has accepted the professorship of chemistry at Emory and Henry College, Emory, Va.

Dr. Simon Klosky has accepted appointment as instructor at the Martin Maloney Chemical Laboratory of the Catholic University of America, Washington, D. C. Dr. Klosky was formerly with the Chemical Warfare Service at Edgewood Arsenal.

Dr. G. Davis Buchner, research chemist at the Agricultural Experiment Station of the University of Kentucky, has secured a year's leave of absence, which he will spend in Europe visiting the more important educational and scientific centers of Italy, Germany, Switzerland, France, and England.

Mr. Thomas H. Wickenden and **Mr. Charles McKnight, Jr.**, have recently joined the development and research department of the International Nickel Co., New York, N. Y., to undertake work in connection with alloy steels.

Mr. J. B. Foote, president and treasurer of Foote Bros. Gear & Machine Company of Chicago, died on October 12, 1922. Mr. Foote was widely known for his skill as a gear maker and inventor for transmission and other machinery. He was the pioneer in making cut steel, case-hardened, tough-cored gears for heavy duty work. He was one of the first to invent and build enclosed types of transmission for reducing electric motor speeds. He shared with Henry Ford the honors of pioneering the present light weight type of farm tractor, and in this connection he was the inventor of the enclosed transmission and live axle drive. He was also the inventor of numerous automatic machines for making cans and was regarded as a foremost authority on special machinery. He is survived by his widow, and his brother, Bradford Foote, who will continue the business of Foote Brothers Gear & Machine Co., 213 N. Curtis St., Chicago, Ill.

Mr. Charles T. Bragg, formerly with the Michigan Smelting and Refining Company, is now president and general manager of the Michigan Valve & Foundry Company.

Dr. Thomas R. Duggan, of the Permutit Co., New York, for many years trustee and chairman of the House Committee of the Chemists' Club, New York, was tendered a dinner on November 3 by about seventy-five members of the Club. The occasion was the departure of Dr. Duggan for an extended visit to England. He sailed November 4 on the Aquitania.

The following instructors and assistant instructors have been added to the chemistry faculty of the University of Kansas: **Robert Taft**, formerly professor of chemistry, Ottawa University; **E. L. Joss**, formerly a member of the faculty of Oklahoma State University; **F. G. Moore**, formerly of Texas Agricultural College; J. M. Wainscott of Southwestern University, Kansas; **William Seaman**, of Brown University; **Miss Helene Thomas, Miss Selma Gottlieb, W. McPherson, A. J. Miller**, and **M. L. Ross.**

Mr. Curtis C. Meigs, formerly president of the consulting chemical engineering firm of Meigs, Bassett, & Slaughter, Inc., with offices at 1304 Finance Building., Philadelphia, Pa., has sold his interest to Bassett & Slaughter, who will conduct the business under the name of Bassett & Slaughter, Inc. Mr. Meigs has taken offices at 709–710, Stephen Girard Building and is associated with Mr. Hugo Schlatter, formerly with the Hercules Powder Co., and Mr. W. B. Goentnerand, who was assistant chief mechanical engineer for the old firm. These men will do consulting work of a chemical engineering nature.

Industrials

The import prohibition on coal-tar products into Italy has been removed; fuel oil has been made duty-free; and important changes are effected in the import duties on coal-tar dyes and intermediates, according to the commercial attaché at Rome. The changes went into effect on October 29. The prohibition on the importation of synthetic dyes and other coal-tar derivatives into Italy went into effect June 3, 1921. Under the present regulations these products may be imported, but at the increased duty of 300 gold lire per 100 kilos instead of the former duty of 120 lire. By the same decree the import duties on nitrobenzol and aniline salts have been raised one-third.

During October 1922 twenty-three companies were formed to engage in the manufacture and distribution of chemicals, drugs, and dyes, with a total indicated investment of $5,950,000, as compared with $5,300,000 in September and $5,850,000 in August. This is slightly below the total capitalization in October 1921, which amounted to $6,675,000.

A joint committee representing the National Association of Wool Manufacturers, the American Association of Worsted and Woolen Manufacturers, and the National Association of Woolen and Worsted Spinners has been named to aid the Bureau of Standards in scientific research work affecting the woolen industry. The committee will meet in Washington in the near future for the purpose of aiding in the drawing up of a program which will more fully utilize the facilities of the bureau in considering general and specific problems of research and standardization in the textile trades.

The Bureau of Labor Statistics has reported a rise of two points in September in the government index number of wholesale prices in chemicals and drugs. The September number is 124, as compared with 122 in August. The chemicals and drugs number is 4.7 per cent below that for September 1921, while the number for all commodities is 8.5 per cent higher.

American industry is spending about $70,000,000 annually on scientific research, according to the Fabricated Production Department of the Chamber of Commerce of the United States. About one-half of this sum is spent by American manufacturers in the conduct of laboratory research, while the remainder is expended in experimental and development work in plants. As a result of scientific research work, approximately $500,000,000 are being saved annually by industry in this country.

As an incentive to members and students of the Canadian Institute of Chemistry resident in Canada, prizes amounting to $75 have been created by three Institute members for the best two articles accepted for publication by any Canadian magazine, which are national in scope and of a business or literary nature. The competition will close May 1, 1923. Prize winners will be chosen by a committee appointed by the council of the Institute.

After extensive investigations of new laboratories now being erected, Dr. Charles E. Coates has submitted to the building committee a plan for the new chemical laboratory to be built at the Louisiana Agricultural College. Approximately $450,000 are available for the erection of this laboratory, and the buildings are to be planned to permit additions when necessary.

At a recent meeting of the directors of E. I. du Pont de Nemours & Co., Inc., it was voted to increase the authorized capital stock from $80,000,000 to $100,000,000, by adding 200,000 shares of $100 par value. The present outstanding capital is $63,378,300, and the directors will declare a 50 per cent stock dividend, with the approval of the stockholders who have been called to meet on December 4 in Wilmington.

The Sales Promotion Section of the Office of Director of Sales, War Department, Washington, D. C., has recently issued a booklet, "War Surplus," which describes the methods resorted to by the War Department in the disposal of its stocks of surplus property, and tells what these stocks contain, where the property is located, and how to buy it. Quartermasters' supplies form the major part of the remaining surplus to be sold, but the Ordnance Department, Air Service, Signal Corps, Medical Department, Chemical Warfare Service, and Corps of Engineers have considerable stocks to be disposed of.

The Chemical Equipment Company is opening a new office at 109 Broad St., New York City, with Mr. G. M. Hickey, formerly of the Celite Products Co., in charge.

It has been announced that the Stauffer Chemical Company is to move its plant from San Francisco to Chester, Pa. Ten acres of land adjacent to the Sinclair Oil Company development have been acquired and several million dollars are to be expended. The buildings alone will cost $500,000.

BOOK REVIEWS

Chemical Technology and Analysis of Oils, Fats, and Waxes. By J. LEWKOWITSCH, M.A., F.I.C. Edited by GEORGE H. WARBURTON. 6th edition. Vol. I, 1921, 682 pp.; Vol. II, 1922, 954 pp. Macmillan & Co., London.

The 5th edition of this work was published in 1913. A great many interesting developments have taken place in the fat and oil industry since that time, which the new edition seems to have covered in a very effective manner. The author very pertinently states in his preface that the greatest progress has been along the lines of the technological side in the development and investigation of new sources of oils and fats, with the hope of furnishing new supplies of food oils. The editor has been able to introduce most of the new material without materially increasing the size of either of the two volumes, and one cannot go through them without realizing that it is a very remarkable piece of work and is undoubtedly the standard book on the subject in the English language.

The first volume covers quite completely the classification of oils and fats, and their methods of analysis and study. The methods of analysis are distinctly English or European methods. The author has largely overlooked the methods of analysis used in this country which have been developed by the Fat and Oil Committees of the American Chemical Society and the American Oil Chemists' Society. In fact, it is the distinct weakness in this book from the standpoint of the American student.

In Chapter 1 the influence of light, moisture, and other materials on the keeping qualities of fat is very important and most complete, and contains the more recent developments on this subject, making it an extremely valuable compilation.

On page 299 there is a statement that the unsaponifiable matters of cottonseed oil contain considerable amounts of sulfur. This statement, from the experience of analysis in this country handling American oils, is certainly incorrect, since a great many tests made on cottonseed oils in this country have shown that they are free from sulfur

Another point where there seems to be a certain amount of confusion is with regard to the titer test as used in the United States. The author seems to think that the Dalican method is accepted in the United States. This, as a matter of fact, is not correct. The method for titer determination is that adopted by the American Association of Official Agricultural Chemists and the Fat and Oil Committee of the American Chemical Society.

The second volume contains only two chapters—one on the commercial preparation of the raw materials used in the fat and oil industries, and the second chapter on the technology of natural oils, fats, and waxes, with methods of preparing, refining, and detecting adulterations. This discussion of the commercial preparation of oils and fats is the weakest part of the book. In fact, only 39 pages are devoted to this subject and almost none of it has any bearing upon modern American practice. The second chapter, however, is practically an encyclopedia of our present knowledge of the composition and adulteration of fats and oils. Practically every known fat and oil are recorded, with information as to its composition, source, and method of preparation, and the present edition shows that there has been a great deal of new material along these lines developed since the previous edition. On page 51 there seems to be a serious error in the tabulation of the American linseed crop for 1915–16–17. Just what these figures should be, it is hard to say.

The only criticism that might be made of the technological side of this book is that the author is evidently not familiar with the cottonseed oil industry or the manufacture of lard in the United States, and has not kept up with the changes in rules that have been made in these industries within the last few years in this country. It seems to me that it would certainly be very desirable for the editor, in future revisions, to get the coöperation of American authorities on these two great oil and fat industries, which are so largely American industries.

L. M. TOLMAN

Handbook of the Petroleum Industry. Vols. I and II. DAVID T. DAY, Editor-in-Chief. 2070 pp. John Wiley & Sons, Inc., New York, 1922. Price, $15.00.

This book has served a valuable purpose in bringing together in two volumes a vast amount of scattered material which in the past has been largely inaccessible to the average oil man. It would have been difficult to pick an editor better qualified for such a task than Dr. Day.

The authors of the various chapters are generally well known in the industry, and speak with authority. This method of compiling is both the strength and weakness of the work. While one author has treated his subject in textbook form, another has followed that of a popular treatise, while still another has followed the real handbook idea in giving formulas, costs, tables, thus furnishing the tools used by the specialist. This lack of balance was doubtless inevitable.

In the preface the editor speaks of our dwindling oil reserve as from five to seven billion barrels. It is not clear why he ignores the exhaustive estimate of nine billions made last year by a representative national committee, nor why it should not have been explained that with rising prices for crude more efficient methods will undoubtedly greatly increase this reserve.

In an otherwise clearly written chapter on the occurrence of oil, in which is included geology, there is a sacrifice of perspective for the sake of tabulation. The author disregards the fine pioneer work of Washburne, McCoy, Roswell Johnson, J. O. Lewis, and others, in their study of the effect of the laws of physical chemistry on problems of migration and accumulation, and merely gives a somewhat elementary synopsis of the anticlinal theory and gravitational separation. The list of occurrences in foreign fields does not reflect the present state of knowledge of those regions.

The chapter on development and production is a remarkably complete description of the tools and material used, and includes many fine illustrations. That phase of the subject dealing with the production of oil from a lease is less good. There is very little of value upon the care of wells, cleaning-out, shooting, and water problems, while a good deal of space is devoted to a popular description of spectacular conditions in the Mexican fields. Operating costs and depletion of a property are not touched upon, nor any mention of acreage yields in various sands and localities. The Smith-Dunn process is unfortunately described as an adaptation of the air-lift system.

One of the best chapters in the book is that upon field geological methods, especially upon the barometric method. It can well be used as a text, and to the geologist is worth the price of the whole book.

The chapter on statistics gives much valuable material. The graphs used are somewhat elementary, and would have been improved by the use of some of the analytical methods, as in Pogue's excellent work, to show relations between consumption and production and prices.

The chapters on transportation, refining, and testing indicate that greater progress has been made in the manufacturing branches of the oil industry than in the art of production. A discussion of costs would have been of value in the chapter on transportation, as is given in that on refining and also in the exceedingly interesting chapter on oil shales. This latter includes a good discussion of market conditions, costs of mining and transportation, character of the oil, by-products and their markets, with a valuable list of occurrences—all of which is very timely.

The chapters on fuel oil, the internal combustion engine, and lubrication leave little to be desired in each field, with their discussions, formulas, and tabulated material. That on pipe is almost entirely from a manufacturer's standpoint. It would be more valuable to the industry if there were some discussion of the use of the various types of pipe and casing in the field. Why is one weight and size used in California and another in Louisiana, and still another in Oklahoma?

The engineer and the chemist must still have several books dealing with different phases of the oil problem on their desks, but among them that by Dr. Day will find a prominent place.

L. G. Huntley

The Origin of Spectra. By Paul D. Foote and F. L. Mohler. A. C. S. Monograph No. 8. 250 pp. Chemical Catalog Co., Inc., New York, 1922. Price, $4.50.

The year 1922 has placed in the hands of spectroscopists several noteworthy books, of which the one under review is important. Foote and Mohler have undertaken, with remarkable success, to correlate the experimental facts of spectroscopy with the general theory of atomic structure which we owe mainly to Planck, Bohr, and Sommerfeld.

How very far away we are from the days of Bunsen, when nearly every new chemical element was being discovered by "spectrum analysis" and when Huggins was learning the composition of the stars; and how far we are also from the days when Kayser, Runge, and Rydberg were first pointing out the orderly series which exists in the chaos of wave lengths, may be realized by considering the remark on page 109, that spectroscopy is the science which is mainly concerned with the interorbital transition of a valence electron which has previously been ejected to an outer orbit.

The Bohr-Sommerfeld atom is accepted frankly and fully. The authors have no hesitation. They possess the courage of their convictions. In many places they point out the need of more information and the difficulty of certain experimental determinations, but never a doubt is entertained concerning the theory.

The first chapter, occupying nearly a quarter of the entire volume, contains a clear exposition of the quantum theory as applied to spectra. The consequences and predictions of the theory are set forth in a manner which is at once striking, unifying, and helpful. The authors never for a moment allow Mendelejeff's table to drop out of their consciousness.

The second chapter dealing with energy diagrams, energy levels, etc., might well have included a little more detail—a little more "connective tissue." A discussion of ionization and resonance potentials follows in Chapter 3; then a fourth chapter concerning line absorption spectra of atoms, full of interest from start to finish. In the fifth chapter is reached the heart of the matter, the emission of line spectra. This is the immediate problem suggested by the well-chosen title of the volume. Here the authors are particularly in the field of their own valuable contributions to knowledge; the discussion is consecutive and exceedingly clear. Later chapters deal with the mooted question of thermal excitation of spectra, with the difficult problem of flame spectra, with thermo-chemical relations, and briefly with X-ray spectra.

Concerning the volume as a whole, it is certain to make considerable demands upon the attention of the reader who desires to distinguish carefully between fact and theory. The authors do not always talk in terms of the laboratory. Ionization and resonance potentials, for example, are defined, not in terms of experiment, but in terms of the dominating model.

The value of the book for reference to recent literature is indicated by the fact that the index of names of authors includes no less than one hundred and seventy-five entries.

The authors have certainly earned the thanks and congratulations of all English-speaking students of spectroscopy; for not only is this volume indispensable to physicists and astrophysicists, but, since the spectrum of an atom is the most characteristic thing about it—not excepting even its atomic weight—the book will prove equally necessary to chemists.

Henry Crew

Clay Products Cyclopedia. Industrial Publications, Inc., Chicago, 1922. 200 pp. Price, $3.00.

This book represents a praiseworthy effort to give to the clay industry information on a large variety of subjects pertaining to ceramics. The nature of the alphabetical and departmental arrangement precludes, of course, the treatment of the many topics in their natural order. The question arises whether it would not be better in future editions to adopt the topical and connected arrangement by chapters as is done in the standard handbooks. The information has been collected from many sources, most of which have been acknowledged, but in several cases this has been overlooked. Such clay-testing methods as are given on pages 142 to 147 might have been eliminated with profit. Misprints, which are difficult to avoid in a work of this kind containing so much tabulated information, are much less numerous than might be expected. The work of compilation has been well done and the book is of real service to the plant executives and operators for whom it is intended.

A. V. Bleininger

Food Products from Afar. By E. H. S. Bailey, Ph.D., and H. S. Bailey, A.B., B.S. 287 pp. The Century Co., New York, 1922. Price, $3.00.

The book is delightfully written and the typographical work, including the reproduction of numerous photographs, is a credit to the printer's craft. Details of the nature and the production or manufacture of foods exotic to the United States are vividly brought to the attention of the reader, be he epicure, nutritionist, or technical chemist. The two former classes may read without danger of being swamped in chemical terms, while the food chemist will find information to aid him in his work for which he would have to search long elsewhere.

After a preliminary chapter on the sociology of foods, are chapters under appropriate captions dealing with Italian pastes, nuts, edible oils, cheese, Arabian and Mediterranean products, rice and spice, foods of the Far East, tropical foods, coffee, Latin-American foods, stimulants and sedatives, bananas, and fish foods, most of which in these days are imported into the United States, and in addition certain unique foods to which the American palate is not as yet trained.

The reviewer feels that the authors, both of whom stand in the front ranks of food chemists, have conferred a greater favor on men of their own calling by writing a book of this character than if they had treated the subject, at this time, from the standpoint of nutritive value or vitamin content.

A. L. Winton

COMMERCE REPORTS

Notice—*Commerce Reports are received by all large libraries and may be consulted there, or single numbers can be secured by application to the Bureau of Foreign and Domestic Commerce, Department of Commerce, Washington, D. C. The regular subscription rate for these Commerce Reports mailed weekly is $3.00 per year (10 cents per single copy), payable in advance to the Superintendent of Documents, Government Printing Office, Washington, D. C.*

October

The new Junquera process for **extracting nitrate of soda** is described. Official tests of the process were witnessed by many men prominent in the nitrate industry, and the impression seems to be general that the inventor has in large part made good his claims. There is a disposition to recognize that a new invention has been made which, when improved, may revolutionize the industry. (P. 23)

Extensive development of steam electric power by utilization of the **lignite deposits** of Italy is being considered under the government subsidy plan for making use of the national fuel resources. (Pp. 26–7)

A recent French decree prohibits the exportation of **uranium ores** from the French colonies and protectorates, except Morocco and Tunis, to countries other than France and its possessions and protectorates. The declared purpose of this decree is to give French chemical manufacturers preferred access to the radium-bearing minerals of Madagascar. (P. 54)

A French decree of September 4, 1922, suspends the maximum duty of 8 francs per 100 kilos hitherto levied on crude **ammonium sulfate** imported into that country. (P. 55)

The Venezuelan government has placed **potassium carbonate, sodium carbonate** and powdered **white marble** on the free list and a duty upon **potassium hydrate** and **sodium hydrate.** (P. 56)

A pronounced shortage of **zinc** exists in Germany at present. Visible stocks are estimated at 8000 metric tons, as compared with 14,000 metric tons a year ago. One of the most important factors said to be responsible for this shortage was the loss of 80 per cent of the former Silesian zinc production to Poland. (P. 73)

Reports from Fitzgerald, Alberta, indicate that **silver** deposits which will equal the silver mines of northern Ontario, have been discovered northeast of that town. It is said to be a high-grade, free-milling ore. (P. 76)

Trial borings for **oil** in northern Kerafuto clearly reveal that the prospects for the production of oil in that region are very good. (P. 95)

The output of **potash** in France during the second quarter of 1922 showed an improvement over that of the preceding quarter, being, respectively, 46,282 and 38,733 tons of pure potash. (P. 98)

The American Embassy at Paris has been informed by the Alsatian Potash Commercial Company that while general conversations are being held relative to a **potash** agreement, no decisions have been reached. (P. 98)

A bill has been introduced in the lower house of the Brazilian Congress which provides for an increase in import duty on **bleaching powder** and on **caustic soda.** (P. 119)

Substances imported into Salvador for the **purification of water** not specified in the customs tariff are to be classed under "Chemical products and industrial preparations," and are subject to duty. (P. 120)

The total production of **petroleum** in the Dutch East Indies during the calendar year 1921 amounted to 2,361,509 metric tons as compared with 2,365,320 tons in 1920 and 2,159,862 tons in 1919. (P. 153)

Increasing interest is being evidenced in the production of **oil** from **bituminous schists** in Italy, production amounting to 16,325 tons in 1920 and 3150 tons in 1921. (P. 153)

The export trade of the United States in **chemicals and allied products** is increasing so rapidly that it is not unlikely the total value for the year will exceed that for 1921. (Pp. 161–2)

A survey of the French manufacture of coloring matters is most discouraging. This same depression appears to be symptomatic of industrial chemicals in general in France. (P. 162)

The new schedule of **German potash** prices is given. (P. 162)

The duty on **copra** exported from New Guinea has been reduced for a period of one year, beginning June 1, 1922. (P. [illegible])

Beginning with September 1922, statistics showing **exports** from the United States, by countries of destination, of certain specified **chemicals** will be issued in mimeographed form by the Bureau of Foreign and Domestic Commerce. (P. 211)

Deposits of **kieselguhr** have recently been discovered near Cheribon, Java, and experiments are being made at several sugar mills to determine whether it can be satisfactorily used in place of the imported product. (P. 211)

Extension of the French **artificial-silk industry** has not kept pace with the increasing French popularity of artificial-silk goods, and the nine mills engaged solely in the manufacture of this material are all booked up for months ahead. (P. 219)

German deliveries of **dyestuffs** to the allied powers are described. An interesting fact is that the largest amounts have been sent to Italy, rather than to France and Belgium as popularly believed. (Pp. 246–7)

The Governor General of the Union of South Africa has proclaimed a **rebate** of the whole or part of the import duty on the following articles, when imported in accordance with certain prescribed regulations and used for certain designated manufacturing purposes: **oils,** used in the lubricating of yarn in the process of weaving, rebate 17 per cent of the duty; **gums** and **turpentines** used in the manufacture of paints, rebate the whole duty on gums and 17 per cent on turpentine; **solvent naphtha, sealite,** and similar **fluxes,** used in the sealing of containers of commodities, rebate the whole duty. (P. 254)

Chlorate of soda and **perchlorate** of **ammonia** are offered to American buyers by a firm in Turin, Italy. Further particulars may be obtained from the Chemical Division of the Bureau of Foreign and Domestic Commerce. (P. 272)

A market for American **fertilizers** is said to exist in the Isle of Pines, and for **ammonium sulfate** at Dunkirk. (P. 272)

"Springbok" motor spirit is the name of a new **gasoline substitute** which has been invented by an attorney of So. Africa. This product is made from the juice of the prickly pear mixed with chemicals. It has been severely tested on various makes of cars and is highly recommended, being noncorrosive, odorless, and equal to or better than gasoline in power and flexibility, a mileage of 22.4 being obtained in a six-cylinder car. (P. 277)

Dr. Edwin Bluemner of Berlin claims to have invented a process for the production of **synthetic benzine.** (P. 278)

It is reported that a professor in one of the German technical schools has been engaged for the last three years in the development of a new process for obtaining **gasoline** from crude oil. The inventor believes that his invention makes possible a production of from 30 to 80 per cent of gasoline from coal tar and bituminous coal, as well as from the hitherto waste crude from which the maximum amount had been obtained under the old systems. (P. 278)

Gonakie, the pods of which produce a **tanning** material of considerable value, is suggested as a possible substitute for sumac. (Pp. 291–2)

The German prices on **unbleached sulfites** have been revised—for the most part downward. (P. 295)

Raw lime and **limestone** may be exported from Czechoslovakia without paying a manipulation fee and without obtaining an export license. (P. 307)

The British Board of Trade has removed the restriction on the exportation of all kinds of **fertilizers** and reimposed the restriction on the exportation of the following **explosives:** Dynobel, Samsonite, and Thames powder. (P. 308)

Special Supplements Issued: Algeria, Haiti, and Venezuela.

CURRENT PUBLICATIONS

NEW BOOKS

Analysis: A Method for the Identification of Pure Organic Compounds. Vol. IV. SAMUEL P. MULLIKEN. 238 pp. Price, $5.00. John Wiley & Sons, Inc., New York.

Artificial Rubber: Künstlicher Kautschuk für Elektrische Isolierungszwecke. KURT GEISLER. 89 pp. Price, $1.00. Verein Deutscher Ingenieure, Berlin

Atomic Form with Special Reference to the Carbon Atom. E. E. PRICE. 148 pp. Price, 5s. Longmans, Green & Co., London.

Belt Conveyors and Belt Elevators. FREDERICK V. HETZEL. 333 pp. Price, $5.00. John Wiley & Sons, Inc., New York.

Camphor: Le Camphre et sa Synthèse. A. DUBOSC. **La Culture Industrielle du Camphrier.** L. TRABUT. 64 pp. Price, 6 fr. Dunod, Paris.

Carotinoids and Related Pigments: The Chromolipoids. LEROY S. PALMER. **American Chemical Society Monograph Series.** 300 pp. Price, $4.50. Chemical Catalog Co., Inc., New York.

Cellulose: Researches on Cellulose. CHARLES F. CROSS AND CHARLES DORÉE. 253 pp. Price, $5.00. Longmans, Green & Co., New York.

Chemistry of To-day. P. G. BULL. 311 pp. Price, 8s. 6d. Seeley Service & Co., Ltd., London.

Colour Index. Part I. F. M. ROWE, EDITOR. 24 pp. Subscription price for the whole work, 84s. Society of Dyers and Colourists, Bradford, England.

Concrete: A Manual of Reinforced Concrete. CHARLES F. MARSH. 4th edition. 504 pp. Illustrated. Price, 21s. net. Constable & Co., Inc., London.

Coal, Coke, and By-Products. 1913–1919. Part III. IMPERIAL MINERAL RESOURCES BUREAU. 173 pp. Price, 7s. H. M. Stationery Office, London.

Dyes: Traité des Matières Colorantes Organiques et de leurs Diverses Applications. EDOUARD EHRMANN. 615 pp. Price, 58 fr. Dunod, Paris

Foundry Practice: A Comparison of British and American Foundry Practice with Special Reference to the Use of Refractory Sands. P. G. H. BOSWELL. 106 pp. Price 4s. 6d. The University Press of Liverpool, Liverpool.

Handbook of Chemical Engineering. DONALD M. LIDDELL. 2 vols. 517 pp. Price, $8.00. McGraw-Hill Book Co., Inc., New York.

Heat: Notes and Examples on the Theory of Heat and Heat Engines. JOHN CASE. 136 pp. Price, $2.50. D. Van Nostrand Co., New York.

Heat Transmission: Technical Records of Explosives Supply 1915–18. No. 9. MINISTRY OF MUNITIONS AND DEPARTMENT OF SCIENTIFIC AND INDUSTRIAL RESEARCH. 48 pp. Price, 5s. 3$^{1}/_{2}$d. H. M. Stationery Office, London.

Inorganic Chemistry: La Chimie des Complexes Inorganiques. ROBERT SCHWARZ. Translated by ANDRÉ JULIARD. 72 pp. Illustrated. Price, 8 fr. Dunod, Paris.

Inorganic Chemistry. E. J. HOLMYARD. 560 pp. Price, $2.00. Longmans, Green & Co., New York.

Organic Chemistry: Cours de Chimie Organique. F. SWARTS. 3rd edition, revised and enlarged. 674 pp. Price, 45 fr. M. Lamertin, Brussels.

Physics: A Concise Physics for Engineering Students. JOHN E. HOYT. 385 pp. Price, $2.50. P. Blakiston's Son & Co., Philadelphia.

Petroleum and Allied Industries. S. KEWLEY. **Industrial Chemistry Series.** 302 pp. Price, $3.50. D. Van Nostrand Co., New York.

Plant Chemistry: An Introduction to the Chemistry of Plant Products. Vol. II. Metabolic Processes. P. HAAS AND T. G. HILL. 140 pp. Price, 7s. 6d. Longmans, Green & Co., London.

Practical Refrigeration for Marine Engineers. H. E. ROBERTS. 87 pp. Price, $1.75. D. Van Nostrand Co., New York.

Quantitative Chemical Analysis. A. C. CUMMING AND S. A. KAY. 432 pp. Price, 15s. Gurney & Jackson, London.

Rubber: The Analysis of Rubber. JOHN B. TUTTLE. **American Chemical Society Monograph Series.** 160 pp. Price, $2.50. Chemical Catalog Co., Inc., New York.

Standard Specifications for Laboratory Apparatus. MANUFACTURING CHEMISTS' ASSOCIATION OF THE UNITED STATES. **Part I. Graduates and Thermometers.** 49 pp. Manufacturing Chemists' Association of the United States, Washington, D. C.

Steel: The Determination of Sulfur in Iron and Steel. H. B. PULSIFER. 160 pp. Illustrated. Price, $2.50. Chemical Publishing Co., Easton, Pa.

Textiles. A. F. BARKER, W. M. GARNER, R. SNOW, W. H. COOK, AND F. BRADBURY. Revised edition. 396 pp. Price, $4.50. D. Van Nostrand Co., New York.

Vanadium, 1913–1919. The Mineral Industry of the British Empire and Foreign Countries. War Period. IMPERIAL MINERAL RESOURCES BUREAU. 19 pp. Price, 6d. H. M. Stationery Office, London.

RECENT JOURNAL ARTICLES

Acid-Resisting Metals and Alloys. GEORGE A. DRYSDALE. *The Coal Industry*, Vol. 5 (1922), No. 10, pp. 452–54.

Adhesive: Sodium Silicate as an Adhesive. REX FURNESS. *Journal of the Society of Chemical Industry*, Vol. 41 (1922), No. 18, pp. 381r–84r.

Application of Artificial Daylight to Laboratory Purposes (Sheringham System). S. H. GROOM. *The Analyst*, Vol. 47 (1922), No. 559, pp. 419–23.

Artificial Silk and Its Applications in the Textile Industry. P. E. KING. *American Dyestuff Reporter*, Vol. 11 (1922), No. 9, pp. 317–18, 329–32.

Artificial Silk: The Manufacture of Artificial Silk. REX FURNESS. *The Chemical Age (London)*, Vol. 7 (1922), No. 174, pp. 522–24.

Bingham Viscometer: The Drainage Error in the Bingham Viscometer. WINSLOW H. HERSCHEL. *Journal of the Optical Society of America and Review of Scientific Instruments*, Vol. 6 (1922), No. 8, pp. 875–98.

Blast Furnace: Bases of Modern Blast Furnace Practice. A. K. REESE. *Blast Furnace and Steel Plant*, Vol. 10 (1922), No. 10, pp. 495–99.

Boiler Tube Slag: How to Combat Formation of Slag on Boiler Tubes. HARRY H. BATES. *American Gas Journal*, Vol. 117 (1922), No. 17 (Whole No. 3372), pp. 370–75.

Ceramic Research: The Organization of a Decorative Ceramic Research Department. FREDERICK H. RHEAD. *Journal of the American Ceramic Society*, Vol. 5 (1922), No. 11, pp. 758–87.

Chrome Tanning. XI. Some Observations on the Properties of the Common Chrome Liquors. D. BURTON, R. P. WOOD, AND A. GLOVER. *Journal of the Society of Leather Trades' Chemists*, Vol. 6 (1922), No. 9, pp. 281–87.

Chrome Tanning: Sur le Tannage au Chrome à un Bain à Partir de l'Alun de Chrome. P. CHAMBARD AND L. MEUNIER. *Journal of the Society of Leather Trades' Chemists*, Vol. 6 (1922), No. 9, pp. 288–96.

Coal Gas: Scrubbing and Condensing Coal Gas. J. R. WOHRLEY. *Gas Age-Record*, Vol. 50 (1922), No. 17, pp. 521–26, 530.

Combustion: Judging the Combustion of Gaseous Fuels from Gas Analyses. A. G. WITTING. *Blast Furnace and Steel Plant*, Vol. 10 (1922), No. 10, pp. 522–28.

Corrosion Control by Deactivation of Water. FRANK N. SPELLER. *Blast Furnace and Steel Plant*, Vol. 10 (1922), No. 10, pp. 500–4.

Corrosion of Cast Iron and Lead Pipes in Alkaline Soils. J. W. SHIPLEY. *Journal of the Society of Chemical Industry*, Vol. 41 (1922), No. 18, pp. 311t–16t.

Dyes: On the Mode of Action of Dyestuffs on Bacteria. F. P. GAY AND T. D. BECKWITH. *American Journal of Hygiene*, Vol. 2 (1922), No. 5, pp. 467–89.

Dyes: The Merchandising of Dyestuffs. ALAN B. CHAFLIN. *American Dyestuff Reporter*, Vol. 11 (1922), No. 8, pp. 261–64.

Fats: La Classification des Corps Gras au Point de Vue Commercial. G. WOLFF. *Chimie et Industrie*, Vol. 8 (1922), No. 3, pp. 544–48.

Gelatin: Progress in the Physical Chemistry of Gelatin. C. R. SMITH. *Journal of the American Leather Chemists Association*, Vol. 17 (1922), No. 10, pp. 508–15.

Glass: From Manganese to Selenium. IRVING E. ADAMS. *The Glass Industry*, Vol. 3 (1922), No. 11, pp. 219–20.

Leather: The Influence of Atmospheric Humidity on the Strength and Stretch of Leather. F. P. VEITCH, R. W. FREY, AND L. R. LEINBACH. *Journal of the American Leather Chemists Association*, Vol 17 (1922), No. 10, pp. 492–507.

Low Temperature Carbonization. S. W. PARR. *Gas Age-Record*, Vol. 50 (1922), No. 17, pp. 531–34.

Manganese Bronze: Occurrence of Blue Constituent in High-Strength Manganese Bronze. E. H. DIX. *Brass World*, Vol. 18 (1922), No. 10, pp. 283–87.

Mechanical Appliances for Pumping Chemical Solutions. A. K. FISCHER. *American Dyestuff Reporter*, Vol. 11 (1922), No. 9, pp. 301-07.

Photography: Studies in Photographic Sensitivity. I—The Distribution of Sensitivity and Size of Grain in Photographic Emulsions. E. P. WIGHTMAN, A. P. H. TRIVELLI AND S. E. SHEPPARD. *Journal of the Franklin Institute*, Vol. 194 (1922), No. 1, pp. 185-220.

Rubber: The Constitution of Rubber. MAITLAND C. BOSWELL. *Canadian Chemistry and Metallurgy*, Vol. 6 (1922), No. 11, pp. 237-43.

Rubber: Testing Rubber Compounded with Zinc Oxide and Litharge. HENRY P. STEVENS. *The Rubber Age*, Vol. 12 (1922), No. 2, pp. 48-49.

Teaching of Science. SIR RICHARD GREGORY. *Science*, Vol. 56 (1922), No. 1451, pp. 433-39.

Turpentine: Composition et Applications Industrielles des Essences de Térébenthine. GEORGES DUPONT. *Chimie et Industrie*, Vol. 8 (1922), No. 3, pp. 549-54.

Zinc: L'Electrométallurgie du Zinc. M. GOJON AND M. LEMARCHANDS. *Chimie et Industrie*, Vol. 8 (1922), No. 3, pp. 506-23.

GOVERNMENT PUBLICATIONS

Notice—*Publications for which price is indicated can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D.C. Other publications can usually be supplied from the Bureau or Department from which they originate.*

Bureau of Mines

Additions, Removals, and Changes in Permissible List of Explosives from March 15 to September 30, Inc., 1922. S. P. HOWELL. *Reports of Investigations* 2402. 3 pp. Issued October 1922.

Explosives Used in August 1922. W. W. ADAMS. *Reports of Investigations* 2404. 5 pp. Issued October 1922.

Fatalities at Coal Mines in August 1922. W. W. ADAMS. *Reports of Investigations* 2399. 3 pp. Issued September 1922.

Fire and Explosion Hazards of Petroleums and Petroleum Products. S. H. KATZ AND N. A. C. SMITH. *Reports of Investigations* 2400. 11 pp. Issued September 1922.

Gunite in Metal Mines (with Tables of Costs and a Bibliography). B. O. PICKARD. *Reports of Investigations* 2397. 30 pp. Issued September 1922.

Operation and Maintenance of Electrical Equipment Approved for Permissibility by the Bureau of Mines. L. C. ILSLEY. *Technical Paper* 306. 23 pp. Paper 5 cents. 1922.

Stripping Problems in Limestone Quarries of the Shenandoah Valley. OLIVER BOWLES. *Reports of Investigations* 2401. 6 pp. Issued October 1922.

Titanium. R. J. ANDERSON. *Reports of Investigations* 2406. 12 pp. Issued October 1922.

Bureau of Standards

Photomicrography of Paper Fibers. R. E. LOFTON. *Technologic Paper* 217. 31 pp. Paper, 5 cents. 1922.

Recommended Specification for Liquid Paint Drier. Prepared and Recommended by the U. S. Interdepartmental Committee on Paint Specification Standardization. September 27, 1920. *Circular* 105. 4 pp. Paper, 5 cents. 1922.

The Decarburization of Ferrochromium by Hydrogen. LOUIS JORDAN AND F. E. SWINDELLS. *Scientific Paper* 448. Paper, 5 cents.

The Preparation of Iron-Carbon-Manganese Alloys and the Effects of Carbon and Manganese on the Mechanical Properties of Iron. R. P. NEVILLE AND J. R. CAIN. *Scientific Paper* 453. Paper, 10 cents. 1922.

Bureau of the Census

Natural Dyestuffs and Extracts. 14th Census of the United States: Manufactures, 1919. Prepared under the supervision of E. F. HARTLEY. 9 pp. 1922.

Smelting and Refining. 14th Census of the United States: Manufactures, 1919. 11 pp. 1922.

Congress

Amending S. Res. 292, directing the Committee on Manufactures to investigate and report to the Senate the conditions of the crude oil and gasoline markets during the years 1920, 1921, and to date in 1922. *S. Res.* 295. Introduced by MR. LAFOLLETTE, April 20, 1922, and referred to Committee to Audit and Control the Contingent Expenses of the Senate; reported without amendment; considered and approved. 3 pp. 1922.

Directing the Committee on Manufactures [illegible] report to the Senate the conditions of the crude oil and gasoline [illegible] the years 1920, 1921, and to date [illegible] *S. Res.* 292. Introduced by MR. MCKELLAR, April 20, 1922 [illegible] 2 pp. 1922.

Extension of the Dye and Chemical Control Act, 1921. *H. R.* 1247. Submitted by MR. [illegible], committed to the [illegible] House, and ordered to be printed. 2 pp. 1922.

Preventing the Oil Pollution of Navigable Waters of the United States. *S. R.* 901. [illegible] 1922.

Tariff Act of 1922 with Index. H. R. 7456, to provide revenue, to regulate commerce with foreign countries, to encourage the industries of the United States, and for other purposes. *H. Doc.* 393. [illegible] pp. 1922.

Tariff Bill of 1922. Conference Report to accompany H. R. 7456. *H. R.* 1207. 162 pp. 1922.

Tariff Bill of 1922. Conference report on the bill (H. R. 7456) to provide revenue to regulate commerce with foreign countries to encourage the industries of the United States, and for other purposes. *S. Doc.* 253. 51 pp. 1922.

To amend Section 35 of the act entitled "An Act to promote the mining of coal, phosphate, oil, oil shale, gas, and sodium on the public domain." *S. R.* 897. Submitted by MR. KENDRICK and ordered to be printed. 2 pp. 1922.

Department of Agriculture

Absorption by Colloidal and Noncolloidal Soil Constituents. M. S. ANDERSON, W. H. FRY, P. L. GILE, H. E. MIDDLETON AND W. O. ROBINSON. *Bulletin* 1122. 20 pp. Paper, 5 cents. Issued October 21, 1922.

Oleoresin Production. A Microscopic Study of the Effects Produced on the Woody Tissues of Southern Pines by Different Methods of Turpentining. ELOISE GERRY. *Bulletin* 1064. 16 pp. Paper, 20 cents. Issued August 21, 1922.

Geological Survey

Cobalt, Molybdenum, Nickel, Tantalum, Titanium, Tungsten, Radium, Uranium, and Vanadium in 1921. F. L. HESS. Separate from Mineral Resources of the United States, 1921, Part I. 27 pp. Published October 23, 1922.

Coke and By-products in 1919–1920. R. S. MCBRIDE AND F. G. TRYON. Separate from Mineral Resources of the United States, 1920, Part II. 77 pp. Published October 18, 1922.

Gold, Silver, Copper, Lead, and Zinc in California and Oregon in 1921. Mines Report. C. G. YALE. Separate from Mineral Resources of the United States, 1921, Part I. 40 pp. Published October 23, 1922.

Secondary Metals in 1921. J. P. DUNLOP. Separate from Mineral Resources of the United States, 1921, Part I. 16 pp. Published October 12, 1922.

Surface Water Supply of the United States, 1918. Part XII. North Pacific Slope Drainage Basins. A—Pacific Basins in Washington and Upper Columbia River Basin. N. C. GROVER, G. L. PARKER AND W. A. LAMB. Prepared in coöperation with the states of Washington and Montana. *Water-Supply Paper* 482. 173 pp. Paper, 15 cents. 1922.

Public Health Service

A Physiological Test for the Activity of Vitamin Preparations. ATHERTON SEIDELL. *Reprint* 762. 5 pp. Paper, 5 cents. 1922.

A Source of Lead Contamination of Cistern Water. Report of an Examination of the Drinking Water Supply System at the U. S. Fish Hatchery Station, Ten Pound Island, Gloucester, Mass., for Possible Sources of Lead Contamination. LEONARD GREENBURG. *Reprint* 772. 5 pp. Paper, 5 cents. 1922.

Control of Drinking and Culinary Water on Vessels in Interstate Traffic. A. E. GORMAN. *Reprint* 764. 8 pp. Paper, 5 cents. 1922.

Sulfarsphenamine. Its Manufacture and Its Chemical and Chemotherapeutic Properties. CARL VOEGTLIN, J. M. JOHNSON AND HELEN DYER. *Public Health Reports*, 37 (November 10, 1922), 2783-98.

The Tannic Acid Method for Quantitative Determination of Carbon Monoxide in the Blood. R. R. SAYERS AND W. P. YANT. *Public Health Reports*, 37 (October 6, 1922), 2433-9.

MANUFACTURERS' TECHNICAL PUBLICATIONS

Metallurgy: Standard Crushing, Grinding, and Pulverizing Mills; Standard Cinder and Metal Reclaiming Mills. Two booklets of 16 pages each dealing with these two important applications of standard mills. STANDARD EQUIPMENT CO., New Haven, Conn.

Industrial Ovens. A booklet of 12 pages describing the sectional type of industrial oven. THE OVEN EQUIPMENT AND MFG. CO., New Haven, Conn.

MARKET REPORT—NOVEMBER, 1922

[Supplied by Drug & Chemical Markets]

Movement of chemical products from producing to consuming channels during November slowed down considerably. Although prices which worked their way to higher levels during September and October might have reacted on a reduction in demand throughout the past month, the generally small stocks of all industrial chemicals and the difficulty in getting shipments through from plants have been sufficient support to prevent any sagging in values. In fact, most sellers have been very bullish and have stiffly maintained prices. Goods available for immediate shipment from distribution points away from manufacturing centers are being held at premiums in some instances, as the railroad car shortage and slow movement of all freight has permitted such stocks to become quite low.

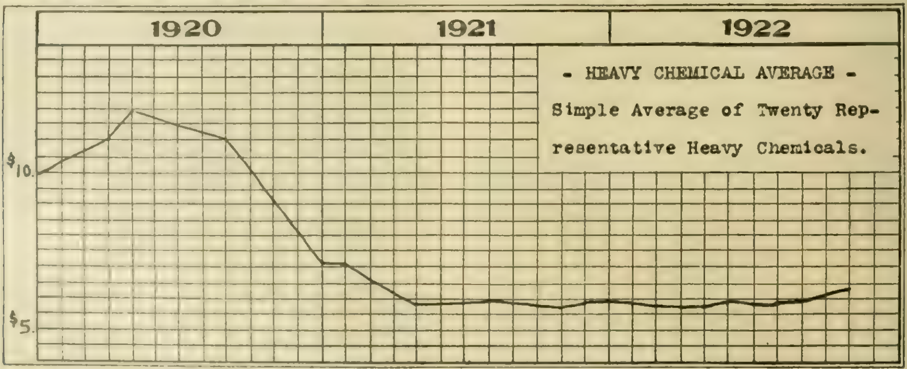
According to reports, the railroads of the country are short about 150,000 freight cars as a result of the recent strike of repairmen, this number of cars being out of commission for want of repairs. The freight embargo, or, as it might better be called, the priority order for food and coal, has caused much difficulty in shipping goods, more particularly in the West and Middle West. The only way to get goods through, according to some reports, is to send a man along with each car to insure its being kept on the move, and not side-tracked and forgotten. Indications point to the fact that thousands of chemical shipments rolling in various parts of the country are virtually lost, consignees being unable to find any trace of goods weeks and months overdue. In the case of a few medicinal products, the situation threatens to become serious.

The advance in price of acetate of lime to 3c per lb. was followed by advances in acetic acid, methanol, formaldehyde, and acetone. Higher cost of production is the main reason for the advance. Mineral acids have been in better demand. Ammonia alums and aluminium sulfate have been very scarce, due to the delayed shipments of bauxite from the South and West. Arsenic is very scarce and prices have advanced. Both foreign and domestic production have been sold and many consumers are still uncovered for the coming season. Copperas has been scarce. Yellow prussiate of soda has declined. Potassium prussiate is strong on scarcity and good demand. Makers are taking on contracts for next year for soda ash, caustic soda, and bichromates at unchanged prices. Caustic and ash are in good demand. The steady advances in the prices of tin, lead, and zinc have resulted in advances in tin crystals, all lead products, and zinc oxide. Higher potash prices have been made by the German Kali Syndicate.

Demand for animal and fish oils has been increasing and stocks are low. Lard oils, tallow, stearic, and oleic acids have advanced in price. Supplies of fish oils were well bought up by soap makers at the close of the fishing season. Menhaden and cod oil are higher. Cottonseed oil has been very active due to scarcity of crude oil and high price of cotton. Linseed oil dropped slightly on reports of a record crop of flaxseed in Argentine. Denatured olive oil is higher. Palm and coconut oils are in good demand. Turpentine advanced to the highest mark in two years at $1.68 per gal., the rise being due to shortage in primary markets.

Coal-tar products as a whole have been very scarce. Since the settlement of the coal strike production has been gaining slowly, but the demand is still much greater than the supply. There has been an increasing demand for 90 per cent benzene for motor fuel, which has cut into the toluene production. Supplies of cresylic acid and phenol are very low and the production of the only large maker is sold far in advance. A few odd lots are found here and there in the open market and the price asked is the highest since 1918. Some imported phenol is now offered at 35c per lb. Rumors are heard to the effect that synthetic phenol plants will soon be in operation as the price of phenol is now high enough to warrant its manufacture at a profit in competition with imported material. The demand for intermediates has been increasing, with greatest interest being shown in H-acid, gamma acid, benzidine, paranitraniline, beta-naphthol and dimethylaniline. Aniline oil is scarce on spot and prices firm. Dimethylaniline is higher on increased cost of raw materials.

In the field of medicinal chemicals less activity has been noted since the first of November. As a contrast to the broad, sharp advances of October, the past month has seen little or nothing happen except in the matter of derivatives of wood alcohol and phenol, which have both continued to skyrocket. Salicylates, strangely, have not moved upward although phenol prices are up close to 50 per cent above their November first level. American refiners have advanced camphor prices. A spot shortage of menthol finds prices on the rise. After the sharp rises in bismuth and mercury preparations in October, the past month has seen a steady demand at unchanged quotations. A number of fine chemicals are being imported from abroad in spite of the higher tariff rates. This is particularly true in rare alkaloids, and in a number of the less common medicinal products.



Courtesy of Drug & Chemical Markets

FIRST-HAND PRICES FOR GOODS IN ORIGINAL PACKAGES PREVAILING IN THE NEW YORK MARKET

INORGANIC CHEMICALS

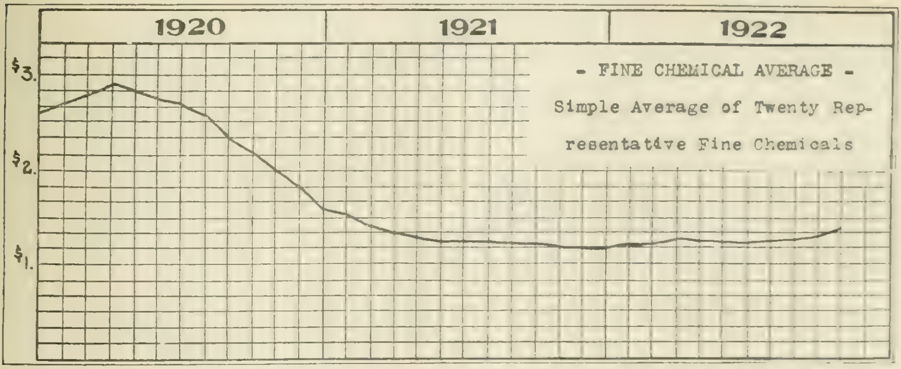
	Nov. 1	Nov. 15	Jan. 1922
Acid, Boric, cryst. bbls.......lb.	.11¾	.11¾	.12¾
Hydrochloric, comm'l. 20° lb.	.01¼	.01¼	.01¼
Hydrofluoric, 30% bbls..lb.	.07	.07	.07
Hydriodic, sp. gr. 1.150...lb.	2.25	2.25	2.00
Nitric, 42°, cbys. c/l wks.lb.	.06½	.06½	.06
Phosphoric, 50% tech.....lb.	.08	.08	.10
Sulfuric, C. P............lb.	.08	.07	.07
66° tks. wks........ton	15.00	15.00	16.00
Oleum 20%.........ton	18.00	18.00	19.00
Alum, Ammonia, lump........lb.	.03½	.03½	.03½
Potash, lump............lb.	*.03	*.03½	*.03½
Chrome.............lb.	.06	.06	.07
Soda, ground............lb.	.03½	.04	.03½
Aluminium Sulfate (iron-free).lb.	.02½	.02½	.02½
Ammonium Carbonate, pwd...lb.	.10¾	.10¾	.08
Chloride, white gran......lb.	.07¾	.07¾	.07½
Ammonia, anhydrous ....lb.	.30	.30	.30
Ammonia Water, drums, 26°...lb.	.07½	.07½	.07½
Arsenic, white...............lb.	.11	.11	.06½
Barium Chloride............ton	*100.00	*100.00	*53.00
Nitrate.................lb.	*.08	*.08	*.07
Barytes, white..............ton	33.50	33.50	28.00
Bleaching Powd., 35%, works ....100 lbs.	2.00	2.00	2.25
Borax, cryst., bbls............lb.	.05½	.05½	.05¾
Bromine, pure, wks...........lb.	.29	.29	.23
Calcium Chloride, fused, f.o.b. N. Y...................ton	24.50	24.50	28.75
Chlorine, liquid..............lb.	.06	.06	.06
Copper Sulfate..........100 lbs.	6.00	6.00	5.55
Iodine, resublimed...........lb.	4.40	4.40	3.80
Lead Acetate, white crystals...lb.	.12	.12	.11
Nitrate.................lb.	.22	.22	.15
Red....................lb.	.08	.09	.08
White (Carb.)............lb.	.08½	.08½	.07¼
Lime Acetate...........100 lbs.	3.00	3.00	1.75
Magnesium Carbonate, tech...lb.	.07½	.07½	.06
Magnesite, calcined..........ton	55.00	55.00	55.00
Phosphorus, yellow...........lb.	*.25	*.25	*.27
Red.....................lb.	*.26	*.26	*.30
Plaster of Paris.............bbl.	4.25	4.25	4.25
Potassium Bichromate........lb.	.10	.10	.10½
Bromide, imported.......lb.	*.19	*.19	*.13
Carbonate, calc., 80-85%.lb.	*.05½	*.05½	*.04½
Chlorate, cryst...........lb.	*.07½	*.08½	*.05½
Hydroxide, 88-92%......lb.	*.06½	*.06½	*.06
Iodide, bulk.............lb.	3.50	3.50	2.90
Nitrate..................lb.	.08	.08	.08
Permanganate, U. S. P....lb.	*.17	*.17	*.15
Prussiate, red............lb.	*.90	*.90	*.29
Yellow...............lb.	*.38	*.39	*.24½
Salt Cake, bulk.............ton	25.00	25.00	17.00
Silver Nitrate...............oz.	.46	.45¾	.44½
Soda Ash, 58%, bags.....100 lbs.	*1.80	*1.80	*1.85
Caustic, 76%, N. Y..100 lbs.	3.75	3.75	3.80

*Resale or Imported (not an American makers' price).

	Nov. 1	Nov. 15	Jan. 1922
Sodium Acetate..............lb.	[illegible]	.07½	.04
Bicarbonate.........100 lbs.	2.00	2.00	2.00
Bichromate..............lb.	.07½	.07½	.07¾
Bisulfite, powd...........lb.	.04¼	.04¼	.04¼
Chlorate..................lb.	.06½	.06½	.07½
Cyanide, 96-98%.........lb.	.23	.23	.28
Fluoride, tech............lb.	.09½	.09½	.09½
Hyposulfite, bbls.......100 lbs.	3.20	3.20	3.50
Nitrate, 95%........100 lbs.	2.40	2.40	2.32½
Nitrite...................lb.	.09	.09	.06½
Prussiate, yellow.........lb.	.23	.22	.16½
Phosphate (di-sod.),tech..lb.	.04½	.04½	.04¼
Silicate, 40°.............lb	.01½	.01½	.01½
Sulfide, 60%, fused.......lb.	.04	.04	.05
Strontium Nitrate............lb.	*.10	*.10	*.10
Sulfur, flowers..........100 lbs.	3.00	3.00	2.75
Crude, mines.......long ton	14.00	14.00	16.00
Tin Bichloride, 50% sol'n......lb.	.10½	.10½	.09¾
Oxide...................lb.	.38	.38	.37
Zinc Chloride, U. S. P.........lb.	.20	.20	.35
Oxide, bbls..............lb.	.07	.07	.08

ORGANIC CHEMICALS

	Nov. 1	Nov. 15	Jan. 1922
Acetanilide, U. S. P. bbls.......lb.	*.30	*.35	*.29
Acid, Acetic, 28 p. c.......100 lbs.	2.92½	2.92½	2.37½
Glacial..............lb.	.11½	.11½	.10
Benzoic, U. S. P........lb.	.60	.60	.60
Carbolic, cryst., U. S. P., drs...............lb.	.30	.35	.12
50- to 110-lb. tins....lb.	.37	.44	.18
Citric, crystals, kegs......lb.	*.50	*.50	*.43
Oxalic, cryst., bbls., wks...lb.	.15	.15	.14
Pyrogallic, resublimed....lb.	1.60	1.60	1.75
Salicylic, U. S. P.........lb.	.35	.35	.24
Tannic, U. S. P., bbls....lb.	.70	.70	.75
Tartaric, cryst., U. S. P...lb.	*.30	*.30	*.25
Acetone, drums...............lb.	.19	.18½	.12
Alcohol, denatured, complete.gal.	.38	.38	.45
Ethyl, 190 proof, bbls....gal.	4.65	4.65	4.75
Amyl Acetate................gal.	2.00	2.00	2.00
Camphor, Jap, refined, cases...lb.	.87	.85	.90
Carbon Bisulfide, c/l..........lb.	.06	.06	.06½
Tetrachloride............lb.	.10	.10	.10½
Chloroform, U. S. P., drums...lb.	.25	.25	.43
Creosote, U. S. P..............lb.	.40	.40	.40
Cresol, U. S. P...............lb.	.18	.18	.14
Dextrin, corn...........100 lbs.	3.09	3.09	2.70
Imported Potato.........lb.	.09	.09	.06½
Ether, U. S. P., 100 lbs.........lb.	.14	.14	.14
Formaldehyde, bbls...........lb.	.13½	.13½	.10½
Glycerol, dynamite, drums....lb.	.17½	.17½	.14½
Methanol, pure, bbls.........gal.	.90	1.02	.75
Methylene Blue, med.........lb.	3.00	3.00	4.00
Petrolatum, light amber......lb.	.04½	.04½	.05¼
Pyridine....................gal.	1.75	1.75	1.75
Starch, corn, pow'd......100 lbs.	2.47	2.47	2.13
Potato, Jap..............lb.	.07	.07	.06½
Sago....................lb.	.03½	.03½	.04



Courtesy of Drug & Chemical Markets

OILS, WAXES, ETC.

	Nov. 1	Nov. 15	Jan. 1922
Beeswax, pure, white.........lb.	.32	.32	.33
Castor Oil, No. 3.............lb.	.12	.12	.10½
Ceresin, yellow...............lb.	.08	.08	.07½
Corn Oil, crude, tanks, mills...lb.	.07¼	.07¼	.06¾
Cottonseed Oil, crude, f. o. b. mill.....................lb.	.08	.08¼	.07
Linseed Oil, raw, c/l.........gal.	.89	.88	.69
Menhaden Oil, crude, mills...gal.	.43	.48	.35
Neat's-foot Oil, 20°..........lb.	.18	.18	.16¾
Paraffin, 128–130 m. p., ref.....lb.	.03¾	.03¾	.05
Rosin, "F" grade, 280 lbs....bbl.	6.95	6.70	5.30
Rosin Oil, first run..........gal.	.43	.43	.36
Shellac, T. N................lb.	.65	.72	.66
Sperm Oil, bleached winter, 38°....................gal.	1.05	1.05	1.70
Stearic Acid, double pressed...lb.	.10	.10	.09¾
Tallow Oil, acidless...........lb.	.10¾	.11¾	.10
Turpentine, spirits of........gal.	1.62	1.57	.82½

METALS

	Nov. 1	Nov. 15	Jan. 1922
Aluminium, No. 1, ingots.....lb.	.20	.22	.17
Antimony, ordinary......100 lbs.	7.00	6.65	4.55
Bismuth......................lb.	2.60	2.60	1.80
Copper, electrolytic..........lb.	.13⅞	.13⅞	.13⅞
Lake.....................lb.	.14	.14	.13¾
Lead, N. Y..............100 lbs.	6.50	7.25	4.70
Nickel, electrolytic...........lb.	.36	.36	.45
Platinum, refined, soft........oz.	108.00	108.00	78.00
Quicksilver, flask......75 lbs. ea.	71.00	71.00	52.00
Silver, foreign................oz.	.69¼	.66½	.65¼
Tin..........................lb.	.35¼	.37½	.32¾
Tungsten Wolframite ...per unit	3.25	3.50	2.00
Zinc, N. Y..............100 lbs.	8.00	8.25	5.20

FERTILIZER MATERIALS

	Nov. 1	Nov. 15	Jan. 1922
Ammonium Sulfate, expt..100 lbs.	3.55	3.55	2.60
Blood, dried, f. o. b. N. Y....unit	4.25	4.35	3.50
Bone, 3 and 50, ground, raw..ton	28.00	28.00	30.00
Calcium Cyanamide, unit of ammonia..................	2.25	2.25	2.25
Fish Scrap, dried, wks......unit	4.25	4.00	3.25 & .10
Phosphate Rock, f. o. b. mine:			
Florida Pebble, 68%.....ton	3.00	3.00	5.00
Tennessee, 78–80%......ton	4.00	4.00	8.00
Potassium Muriate, 80%....unit	.70	.70	*.75
Tankage, high-grade, f. o. b. Chicago...............unit	4.50 & .10	4.35 & .10	3.00 & .10

COAL-TAR CHEMICALS

Crudes

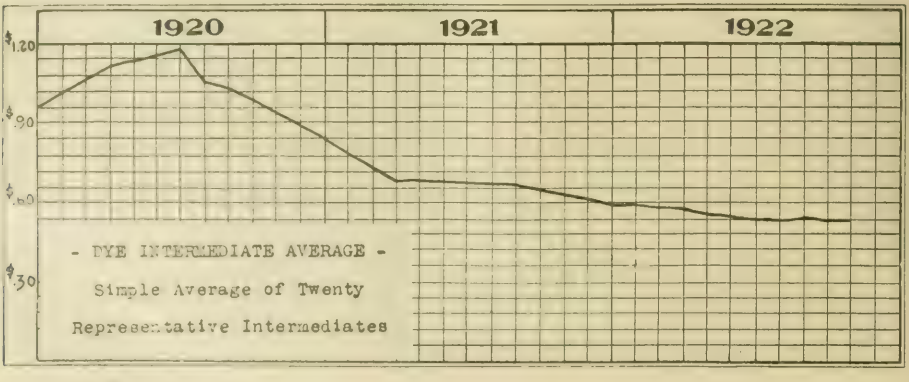
	Nov. 1	Nov. 15	Jan. 1922
Anthracene, 80–85%.........lb.	.75	.75	.75
Benzene, pure, tanks ....gal.	.30	.30	.29
Naphthalene, flake............lb.	.06½	.06½	.07½
Phenol, drums................lb.	.30	.33	.11

Crudes (*concluded*)

	Nov. 1	Nov. 15	Jan. 1922
Toluene, pure, tanks.........gal.	.30	.30	.30
Xylene, 2 deg. dist. range, tanks.................. gal.	.45	.45	.45

Intermediates

	Nov. 1	Nov. 15	Jan. 1922
Acids:			
Anthranilic...............lb.	1.10	1.10	1.10
Benzoic, tech.............lb.	.50	.50	.50
Cleve's...................lb.	1.50	1.50	1.50
Gamma.....................lb.	1.80	1.80	2.25
H.........................lb.	.75	.75	1.00
Metanilic.................lb.	1.00	1.00	1.60
Monosulfonic F...........lb.	2.30	2.30	2.80
Naphthionic, crude.......lb.	.60	.60	.65
Nevile & Winther's.......lb.	1.20	1.15	1.30
Picric....................lb.	.20	.20	.25
Sulfanilic................lb.	.17	.17	.26
Tobias'...................lb.	1.50	1.50	2.00
Aminoazobenzene............lb.	1.15	1.15	1.15
Aniline Oil.................lb.	.16	.16	.17
Aniline Salt................lb.	.24	.24	.25
Anthraquinone (sublimed)....lb.	1.35	1.35	1.50
Benzaldehyde, tech...........lb.	.65	.55	.45
U. S. P...................lb.	1.40	1.40	1.25
Benzidine Base...............lb.	.85	.85	.90
Benzidine Sulfate............lb.	.70	.70	.70
Diaminophenol...............lb.	3.75	3.75	5.50
Dianisidine..................lb.	4.50	4.50	4.75
p-Dichlorobenzene...........lb.	.06	.06	.15
Diethylaniline...............lb.	.60	.60	.90
Dimethylaniline..............lb.	.38	.41	.40
Dinitrobenzene...............lb.	.20	.20	.21
Dinitrotoluene...............lb.	.20	.20	.25
Diphenylamine................lb.	.52	.52	.58
G Salt.......................lb.	.65	.65	.70
Hydroquinol..................lb.	1.15	1.15	1.35
Monochlorobenzene...........lb.	.08	.08	.10
Monoethylaniline.............lb.	1.00	1.00	1.00
b-Naphthol, dist.............lb.	.24	.24	.30
a-Naphthylamine.............lb.	.30	.30	.30
b-Naphthylamine.............lb.	.95	.95	1.05
m-Nitroaniline..............lb.	.62	.62	.85
p-Nitroaniline..............lb.	.73	.73	.77
Nitrobenzene (Oil Mirbane)...lb.	.10	.10	.10
p-Nitrophenol...............lb.	.72	.72	.75
o-Nitrotoluene..............lb.	.09	.09	.15
p-Nitrotoluene..............lb.	.60	.60	.70
m-Phenylenediamine.........lb.	.90	.90	1.10
p-Phenylenediamine..........lb.	1.50	1.50	1.60
Phthalic Anhydride..........lb.	.35	.35	.38
R Salt......................lb.	.55	.55	.60
Resorcinol, tech.............lb.	1.30	1.30	1.50
U. S. P...................lb.	2.00	2.00	2.00
Schaeffer's Salt. ....lb.	.60	.60	.70
Sodium Naphthionate........lb.	.60	.60	.70
Thiocarbanilide.............lb.	.35	.35	.40
Tolidine (base)..............lb.	1.15	1.15	1.20
Toluidine, mixed.............lb.	.30	.30	.30
o-Toluidine..................lb.	.14	.14	.20
p-Toluidine..................lb.	.95	.95	1.10
m-Toluylenediamine..........lb.	.95	.95	1.10
Xylidine.....................lb.	.42	.42	.40



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